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SYNTHESIS, CHARACTERISATION  
AND CONFORMATIONAL STUDIES OF  
SIX MEMBERED PLATINACYCLES

by

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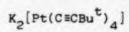


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# ABBREVIATIONS

br	broad
1,5-COD	cycloocta-1,5-diene
C.I.	Chemical Ionisation
Cp	cyclopentadienyl
Cp'	pentamethylcyclopentadienyl
d	day
DMSO	dimethylsulphoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
E.I.	Electron impact
Ep	Electrode potential
h	hour
i	current
Infrared; s	strong
m	medium
L	ligand
min	minute
N.m.r.	Nuclear magnetic resonance
N.m.r.; s	singlet
d	doublet
m	multiplet
t	triplet
v	speed rate

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## ABSTRACT

Some novel platiniacyclohexanes have been prepared and characterised by n.m.r. methods and the conformations of the six membered rings investigated by variable temperature n.m.r. studies and single crystal X-ray diffraction techniques. The platiniacyclic ring in compound  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2)_5]$  adopts a half chair conformation in the solid state whereas the substituted ring in compound  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$  exists in a skew conformation.

In low temperature solution n.m.r. studies ( $\sim 150^\circ\text{C}$ , 400 MHz), the slow exchange limit has not been observed indicating an upper limit of  $\Delta G^\ddagger$  of ca  $20\text{ kJ mol}^{-1}$  for the barrier to ring reversal.

A series of 9,10-dihydro-9-platinaanthracenes  $[\text{L}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  ( $\text{L} = \text{PEt}_3$ ,  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$ ,  $\text{dppe}$ ,  $\text{dppe}$ , 1,5-COD) have been prepared and characterised by n.m.r. methods and conformational studies of the platiniacyclic rings carried out.  $^1\text{H}$  n.m.r. studies have shown that when  $\text{L} = \text{PEt}_3$ ,  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$ ,  $\text{dppe}$ , the rings are rigid in solution. Less sterically demanding ligand allows rapid ring reversal to take place in solution.

The platiniacyclic ring in compound  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  adopts a boat conformation in the solid state and variable high temperature n.m.r. studies indicate that this structure is rigidly maintained in solution. The coalescence temperature for the ring reversal process was not reached ( $< 100^\circ\text{C}$ , 90 MHz) showing that the energy barrier,  $\Delta G^\ddagger > 70\text{ kJ mol}^{-1}$ .

Oxidative addition of Iodine to compound  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  gives the platinum(IV) compound  $[(\text{PEt}_3)_4\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$ .  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy show the phosphine ligands are in a trans arrangement. X-ray crystal structure analysis confirmed this and shows that the ring adopts a flattened boat conformation in the solid state.  $^1\text{H}$  n.m.r. studies show that the ring is fluxional in solution. In low temperature n.m.r. studies a value of  $\Delta G_{\text{TC}}^\ddagger = 40.5 \pm 0.4\text{ kJ mol}^{-1}$  was

calculated for the barrier to ring reversal.

Repeated attempts to obtain a fully unsaturated 'platina-anthracene' moiety from either the platinum(II) or platinum(IV) precursors were unsuccessful.

A series of cis and trans bis-phosphine complexes of the type,  $[MX_2(Ph_2PCH_2CH_2CH_2OH)_2]$  ( $M = Pt, X = Cl, Br, I, CH_3$ ) and  $[MXX'(Ph_2PCH_2CH_2CH_2OH)_2]$  ( $M = Pt, X = Cl, X' = CH_3, M = Pd, X = X' = Cl$ ) are prepared and characterised by  $^{31}P$ - $^1H$  and  $^1H$  n.m.r. and infra-red spectroscopy. Addition of  $AgClO_4$  to cis- $[PtCl_2(Ph_2PCH_2CH_2CH_2OH)_2]$  gives the air stable bis-alcohol chelate cis- $[Pt(Ph_2PCH_2CH_2CH_2OH)(ClO_4)]_2$ . Either of these cis complexes can be deprotonated to give the air stable bis-alkoxo complex  $[Pt(Ph_2PCH_2CH_2CH_2O)_2]$ . The general instability of monodentate alkoxo-platinum complexes is attributed to facile  $\delta$ -hydrogen elimination and not to abnormally weak Pt-O bonds. The chemistry of the Pt-O bonds in the bis-alkoxo complex has been investigated by reaction with  $HCl$ ,  $SO_2$  and 2,6-dimethylphenylisocyanide.

Tetraacetylido complexes of the type  $M'_2[Pt(C\equiv CR)_4]$  ( $M' = K^+, R = Ph, Bu^t$ ;  $M' = [N(PPh_3)_2]^+$ ,  $R = CO_2Me, CO_2Et$ ) are prepared by new routes. The X-ray structure of compound  $K_2[Pt(C\equiv C Bu^t)_4]$  as its 28  $H_2O$  solvate has been determined. The bulky tert-butyl groups prevent stacking of the  $[Pt(C\equiv C Bu^t)_4]$  groups into chains.

**DECLARATION**

The work described in this thesis is the original work of the author except where acknowledgement is made to work and ideas previously published. It was carried out in the Department of Chemistry, University of Warwick, between October 1984 and September 1987, and has not been submitted previously for a degree at any institution.

#### ACKNOWLEDGEMENTS

I would like to thank the Chairman of the Department of Chemistry, Professor M.G.H. Wallbridge for the use of departmental facilities.

I am indebted to Drs N. Alcock and M. Pennington for the determination of the X-ray crystal structures, and Drs G. Howarth and A. Harrison for their assistance in the variable temperature n.m.r. studies. I would also like to thank Dr P. Bartlett for his assistance in the electrochemistry. I thank Dr. G. Semple for the proof reading of this work.

Above all, I would like to thank my supervisor, Dr F.G. Pringle for his guidance and encouragement during the course of this work.

Finally, I thank S.E.R.C. for their financial support.

## CHAPTER ONE

## METALLACYCLOALKANES AND METALLACYCLOALKENES

## 1.1 INTRODUCTION

In recent years heterocycles containing transition metals have been the subject of considerable interest. This is especially so for metallacycloalkanes (1.1) which are fully saturated and metallacycloalkenes which contain at least one unsaturated bond.


 $n = 1, 2, 3$ 

(1.1)

These compounds have been recognised as intermediates in a number of stoichiometric and catalytic reactions, e.g. alkene metathesis,<sup>1-4</sup> isomerisation of strained carbocyclic rings<sup>5,6</sup> and cycloaddition of alkenes.<sup>7,8</sup> Metallacyclopentane and metallacyclopentadiene complexes have been extensively investigated and found to be important intermediates in alkene and alkyne oligomerisation.<sup>9,10</sup> As a result, they have been used in the synthesis of dienes,<sup>11,12</sup> substituted pyridines<sup>13,14</sup> and cyclic ketones.<sup>15,16</sup>

Although the labile nature of these intermediates often make their study difficult, this has not inhibited the extensive research into the more stable, often non-catalytic metallacycles.

The non-catalytic metallacycles have also been recognized as a potentially useful class of organometallic compounds undergoing some novel reactions. It is the observation that metallacycles containing two metal carbon  $\sigma$  bonds are relatively stable that has stimulated the detailed study of their chemistry.<sup>17,18</sup>

Two comprehensive reviews<sup>17,18</sup> have been published of metallacycloalkanes and metallacycloalkenes covering the methods for synthesis, the structures, and the physical properties of these compounds. The most recent review covers the literature up to 1985.<sup>18</sup> The following sections of this work will briefly cover the important aspects of metallacycles up to the end of 1987 with emphasis on recently reported work.

## 1.2 METHODS FOR SYNTHESIS OF METALLACYCLOALKANES

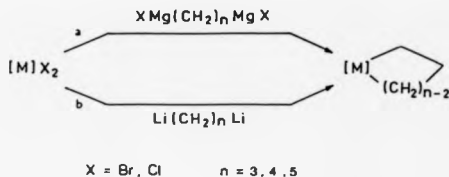
### 1.2.1 Anionic or Cationic Alkylation of Metal Complexes

A general and widespread method used for synthesis of metallacycloalkanes of different ring size for a range of transition metals is reaction of the metal dihalide complex with either dithioalkane or bis(bromomagnesium)alkane reagents (Scheme 1.1).

Typical examples of compounds made by this procedure are metallacyclobutanes, -pentanes, -hexanes or -heptanes of titanium,<sup>19,20</sup> rhenium,<sup>21</sup> cobalt,<sup>22,23</sup> rhodium,<sup>24,25</sup> iridium,<sup>22,24</sup> platinum,<sup>26</sup> palladium,<sup>27,28</sup> nickel,<sup>29</sup> molybdenum<sup>30</sup> and tungsten.<sup>30</sup>

Cationic alkylation of metal Lewis bases can also lead to the formation of metallacycles. For example, the anion  $[\text{CpRe}(\text{CO})_2]^{2-}$

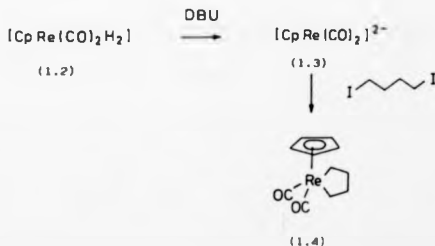




Scheme 1.1. Preparation of metallacycloalkanes by treatment of a metal dihalide with either bis(bromomagnesium) alkane (a) or dilithioalkane (b).

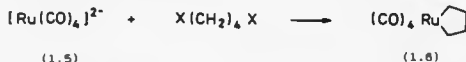
(1.3) obtained by deprotonation of  $[\text{CpRe(CO)}_2\text{H}_2]$  (1.2) with the base 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), reacts with 1,4-diiodobutane to give the rhenacyclopentane (1.4)<sup>31,32</sup> (eq. 1.1).

eq. 1.1



A simple route to a ruthenacyclopentane (1.6)<sup>33</sup> is the reaction of butanediy bis(trifluoromethanesulphonate) with  $[\text{Ru}(\text{CO})_4]^{2-}$  (1.5) (eq. 1.2).

eq. 1.2



#### 1.2.2 Intermolecular Insertion of a Metal into a Carbon-Carbon Bond

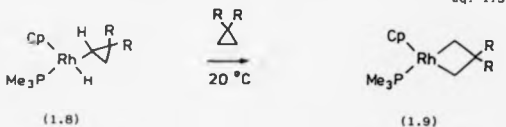
The first metallacyclic complex prepared by Tipper in 1955,<sup>34</sup> was obtained by insertion of platinum into a carbon-carbon bond of a cyclopropane ring. Similarly, Ziese's dimer  $[\text{Cl}_2\text{Pt}(\text{C}_2\text{H}_4)]_2$  reacts with a variety of substituted cyclopropanes to yield polymeric metallacyclobutane products. When these polymeric compounds are treated with an excess of ligands L (e.g. L = Pyridine), a monomeric metallacyclobutane (1.7) precipitates.<sup>35</sup> The most stable isomer thermodynamically, has the platinum atom bonded to the least substituted carbon atoms with the formation of the metallacyclobutane occurring with retention of stereochemistry in the cyclopropane.<sup>36</sup>



(1.7)

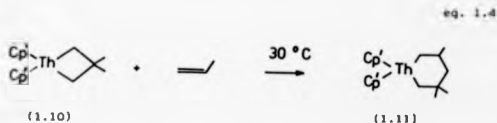
### 1.2.3 Intramolecular Insertion of a Metal into a Carbon-Carbon Bond

The hydridocyclopropylrhodium complex (1.8) decomposes rapidly at temperatures above 0°C to the rhodacyclobutane (1.9) (eq. 1.3).<sup>37</sup> The rearrangement is intramolecular, regiospecific and occurs by insertion of the [CpRhL] unit into the  $\alpha$ -carbon-carbon bond of the cyclopropyl ring. Insertion is always into the less highly substituted  $\alpha$ -carbon-carbon bond. Rhodacyclopentanes have been prepared in a similar manner from the hydridocyclobutyl rhodium complexes.<sup>38</sup>



### 1.2.4 Insertion of an Alkene into a Metal-Carbon $\sigma$ Bond

A thoracyclohexane (1.11)<sup>39</sup> has been prepared by reaction of thoracyclobutane (1.10) with propylene which involves insertion of the C=C double bond into the Th-C bond (eq. 1.4).



The n.m.r. spectroscopic data of (1.11) is in accord with the thoracyclohexane ring adopting a chair conformation in solution.

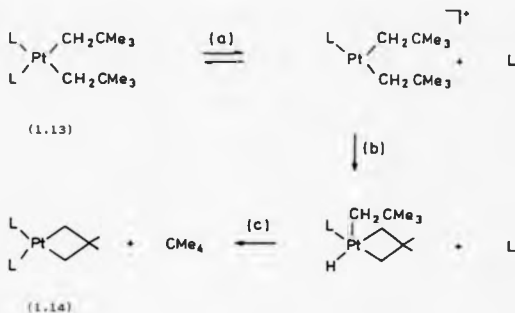
Insertion of ethylene into the Th-C bond of (1.10) results in the formation of (1.12) which is less thermally stable than (1.11).



(1.12)

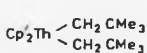
#### 1.2.5 Cyclometallation Reactions of Metal Dialkyl Complexes

Several metallacycloalkanes have been formed by cyclometallation reactions of metal dialkyl complexes.<sup>40-45</sup> For example, the platinumacyclobutane (1.14) is cleanly formed in an intramolecular  $\gamma$ -C-H activation process involving the neopentyl ligands in compound (1.13). The mechanism (A) of formation of (1.14) (Scheme 1.2) involves: a) dissociation of a phosphine ligand to form a vacant coordination site on the platinum metal; b) intramolecular oxidative addition of the methyl C-H bond of a neopentyl ligand to platinum; c) reductive elimination of neopentane.



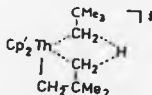
Scheme 1.2. Cyclometallation mechanism proposed for bis(phosphine) platinum dialkyl complexes.

In contrast, thermal cyclometallation of  $[\text{Cp}'_2\text{Th}(\text{CH}_2\text{CMe}_3)_2]$  (1.15) proceeds unimolecularly<sup>46,47,48</sup> to form the thoracyclobutane (1.16) and neopentane (eq. 1.5). The mechanism (B) involves a concerted heterocyclic process with hydrogen atom abstraction and metallacycle formation occurring in a four-centre transition state.

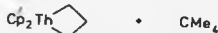


(1.15)

50 °C



eq. 1.5



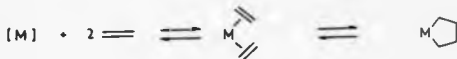
(1.16)

The difference in the cyclometallation mechanisms is due to the fact that early transition metals and f-element centres (such as thorium) are in high oxidation states and often do not possess energetically accessible oxidation states for the oxidative-addition/reductive-elimination sequences present in mechanism (A).

#### 1.2.6 Coupling Reactions of Alkenes

A method for synthesis of metallacyclopentanes is the reaction of a metal complex with alkenes<sup>49</sup> (eq. 1.6). The coupling of two alkenes in the coordination sphere of a transition metal leading to formation of metallacyclopentanes has been investigated theoretically.<sup>50</sup> Metallacyclopentanes have been shown to be key intermediates in metal catalysed cycloadditions and cycloreversions of alkenes.<sup>8,51-55</sup>

eq. 1.6



Recently Binger *et al.*<sup>56</sup> synthesised the first unsymmetrical nickelacyclopentane (1.17) formed by coupling two different alkenes at the metal centre (eq. 1.7).

eq. 1.7



(1.17)

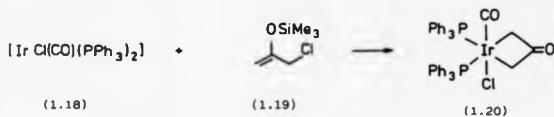
### 1.2.7 Synthesis of Functionalised Metallacycles

Kemmitt *et al.*<sup>57-61</sup> have synthesised a series of closely related four membered metallacycles which are functionalised in the 3-position to give metallacyclobutanones.

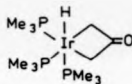
Metallacyclobutan-3-one complexes of platinum,<sup>57,59</sup> palladium,<sup>58</sup> iridium<sup>61</sup> and osmium<sup>61</sup> have been made by several novel methods. For example, treatment of *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (1.18) with the silylenol ether (1.19) gives the iridacyclobutan-3-one

(1.20) (eq. 1.8). Platinum and osmium metallacyclobutan-3-ones have also been made by this route.

eq. 1.8



The closely related iridacyclobutan-3-one (1.21) was prepared by Tulip *et al.*<sup>62</sup> by reaction of  $[\text{Ir}(\text{PMe}_3)_4\text{Cl}]$  with the enolate salt of acetone.

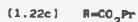
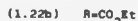
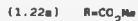
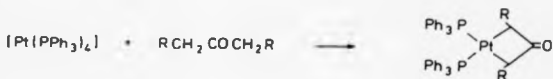


(1.21)

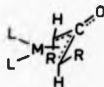
Substituted platinacyclobutan-3-ones (1.22a-c) have been prepared by reaction of the platinum(0) compound  $[\text{Pt}(\text{PPh}_3)_4]$  with dialkyl-3-oxopentanedioates (eq. 1.9).<sup>59</sup>



eq. 1.9



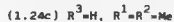
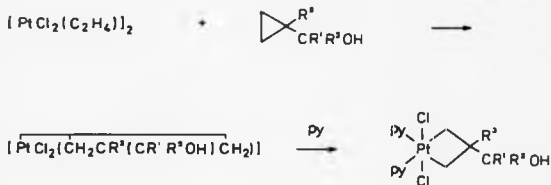
The studies on metallacyclobutan-3-ones of platinum<sup>57,59</sup> and palladium<sup>58</sup> suggest that the bonding descriptions should include a contribution from the slipped  $\eta^2$ -oxodimethylenemethane structure (1.23).



(1.23)

Puddephatt *et al.*<sup>63</sup> have synthesised alcohol substituted platynacyclobutanes (1.24a-d) by treatment of Ziese's dimer  $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$  with the appropriately substituted cyclopropane followed by addition of pyridine ligands (eq. 1.10).

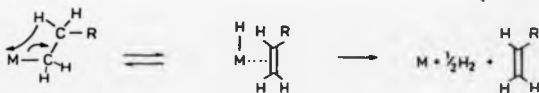
eq. 1.10



### 1.3 STABILITY OF METALLACYCLOALKANES

The thermal stability of metallacycloalkanes is a feature which is useful in that it allows this class of compound to be studied in greater detail.<sup>63</sup> The thermal stability associated with many transition metal alkyls is thought to be kinetic in origin. It is not that the transition metal carbon  $\sigma$  bonds are thermodynamically weak (bond energies range ca<sup>64</sup> 160-350 kJ mol<sup>-1</sup>), but that several low energy pathways are available for their decomposition.<sup>65</sup> The dominant decomposition pathway of most acyclic transition metal alkyls is  $\beta$ -hydrogen elimination<sup>65</sup> (eq. 1.11).

eq. 1.11



Whitesides et al.<sup>26,66</sup> have shown that four- five- and six-membered platinacycles are more stable than the corresponding cis-di-n-alkylplatinum(II) compounds.<sup>67-70</sup> This is true for all metallacycles of these sizes.<sup>66</sup>

The enhanced stability of the metallacycles is due to two factors: (i) the principal decomposition pathway,  $\beta$ -hydrogen elimination is suppressed since the M-C-C-H dihedral angles in these compounds are constrained to values far from the optimal  $0^\circ$ ;<sup>66</sup> (ii) the chelate effect.<sup>71</sup> Metallacycles of larger ring size have lower stability however, because the ring is more flexible leading to a more sterically favourable transition state for  $\beta$ -hydrogen transfer and a smaller chelate effect exists.<sup>71</sup>

An important consequence of the suppression of  $\beta$ -hydrogen elimination by incorporation of alkyl groups into metallacycles is that other potentially valuable types of reactions such as carbon-carbon bond formation<sup>72-75</sup> and cleavage<sup>15,20,29,76</sup> can be observed. For example, in the thermal decomposition of titanacyclopentane (1.25) a transition state with an M-C-C-C dihedral angle of about  $0^\circ$  is present and a carbon-carbon bond cleavage reaction takes place producing ethylene<sup>20</sup> (eq. 1.12). The  $\beta$ -hydrogen elimination reaction also takes place producing but-1-ene.

eq. 1.12



(1.25)

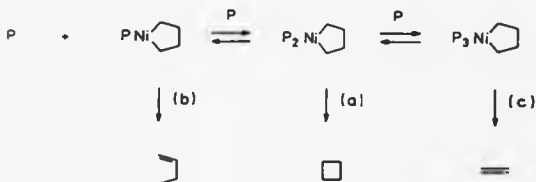
The formation of ethylene from metallacyclopentanes has been studied theoretically by Hoffmann *et al.*<sup>50,77</sup> and has been found to be a symmetry allowed reaction for titanacyclopentane (1.25) (eq. 1.13).

eq. 1.13



(1.25)

Grubbs *et al.*<sup>78-80</sup> have shown that depending on the coordination number of the nickel, nickelacyclopentanes undergo three major reactions: (a) reductive elimination with carbon-carbon bond formation to give cyclobutanes, (b)  $\beta$ -hydrogen elimination resulting in the formation of but-1-ene and (c) carbon-carbon bond cleavage to give ethylene (Scheme 1.3).



Scheme 1.3. Thermal decomposition of nickelacyclopentanes with differing coordination numbers.

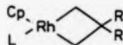
#### 1.4 X-RAY CRYSTAL STRUCTURES OF METALLACYCLOBUTANES AND METALLACYCLOPENTANES

A number of crystal structures have been determined for four and five membered metallacycloalkanes for a range of transition metals.<sup>13,14,32,37,41,44,63,81-93</sup> In contrast no crystal structure determination of a metallacyclohexane, prior to this work, has been reported.

Two important structural parameters of metallacycloalkanes which are involved in catalytic reactions are the conformation of the ring and the ease of distorting the ring toward potential reactive intermediates.<sup>81</sup> Structure-reactivity studies therefore have an important role in understanding metallacycle chemistry.

The conformations of the metallacyclosilanes are varied and are dependent not only on the nature of the metal but on the presence and number of substituents on the ring and the steric requirements of the other ligands.

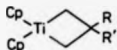
Metallacyclobutanes may adopt planar<sup>37</sup> or nearly planar conformations or puckered conformations<sup>90</sup> which may either be symmetrical or unsymmetrical. For example, in the rhodacyclobutane<sup>37</sup> (1.26a) the ring is essentially planar and symmetrical about the Rh-C axis, whereas in the substituted compound (1.26b) the ring is puckered.<sup>90</sup> It is thought that puckering reduces steric interaction of the phosphine ligand with the cyclopentadienyl ligand and the methyl groups on the ring.



(1.26a) L =  $\text{PMe}_3$ , R = H

(1.26b) L =  $\text{PPh}_3$ , R = Me

The metallacyclobutane rings in the compounds (1.27a-c) are nearly planar and symmetrical.<sup>71</sup> The steric interaction between the R group and the cyclopentadienyl ligand is relieved by a rocking motion of the C(3) fragment in the plane instead of puckering.



The titanacyclobutanes have been demonstrated to be intermediates in the alkene metathesis reaction.<sup>94</sup> A highly distorted metallacycle may be expected if the metal-alkylidene-alkene structures (eq. 1.14), are involved in the reaction as calculations suggest.<sup>95</sup>

eq. 1.14



The deuterium isotope effects on carbon chemical shifts of the titanacyclobutanes in solution are consistent with a symmetric but easily distorted metallacycle structure. It is proposed that the symmetrical titanacyclobutane rests at the minimum of a broad potential surface so that distortion toward the required transition state is facile.

Several crystal structures have been determined for a series of platinacyclobutanes,<sup>96</sup> and in many the platinacyclobutane ring is found to be puckered. The ring strain in platinacyclobutanes is thought to be lower than in cyclobutane because the Pt-C bond is longer than the C-C bond.<sup>97</sup> The degree of non planarity of the Pt-C<sup>1</sup>-C<sup>2</sup>-C<sup>3</sup> ring system can be measured by the fold angle between planes [C(1)-Pt-C(3)] and [C(1)-C(2)-C(3)]. The puckering in platinacyclobutanes is in the range 0-30°.

For example, the ring in (1.28) is almost completely planar<sup>98</sup> with a fold angle of 3°. In the platinum(IV) derivative (1.29) the ring is planar (fold angle 0°), indicating that oxidative addition of chlorine to (1.28) occurs with minimal structural reorganization.



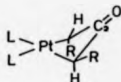
(1.28)



(1.29)

The platinacyclobut-3-ones appear to contain rings which are highly puckered.<sup>59</sup> For example, the fold angle in (1.22a) is 54.4°(4). Cyclobutanone itself is only slightly non planar.





(1.22a)

A consequence of the large fold angle is that the Pt-C(2) distance is such that there is considerable orbital interaction between Pt and C(2). It is the presence of the coordinatively unsaturated platinum centre and an unsaturated ring carbon atom in (1.22a) leading to a transannular Pt...C bonding interaction that is an important factor in accounting for the ring puckering. Similar puckering of this ring is observed in the metallacyclobutan-3-ones of palladium(II)<sup>58</sup> and iridium(III).<sup>61</sup>

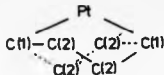
Crystal structures show that metallacyclopentanes may adopt either a symmetrical<sup>86</sup> or unsymmetrical<sup>87</sup> puckered conformation or an opened-envelope conformation.<sup>82</sup>

The structure of  $[\text{Pt}(\text{CH}_2)_4(\text{PPh}_3)_2]$  (1.30)<sup>86</sup> shows an unsymmetrical puckering of the platinacyclopentane ring which does not arise from crystal packing requirements, but may indicate the mechanism whereby rearrangement of metallacyclic intermediates in alkene metathesis reactions could occur.



(1.30)

In comparison the structure of the 18-electron platinum(IV) complex  $[\text{PtI}_2(\text{CH}_2)_4(\text{PMe}_2\text{Ph})_2]$ <sup>87</sup> shows symmetrical puckering of the ring. The puckering of the ring relieves the crowding of the hydrogen atoms on adjacent carbon atoms. Disorder is also observed in the ring as a result of the two central carbon atoms alternating between two forms as indicated in (1.31).



(1.31)

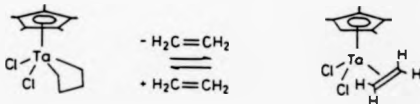
The first example of an opened-envelope conformation of a metallocyclopentane ring was reported for the tantalum compound (1.32).<sup>82</sup>



(1.32)

The opened-envelope conformation is preferred over the puckered conformation possibly because there is a limited cone angle of space available to the ligand at the tantalum atom centre. Puckering of the ring would lead to considerably more interaction between the metallacyclopentane ring and the pentamethylcyclopentadienyl ligand. The orientation of the ring may, in some way facilitate the observed reversible loss of alkene from this class of compound.<sup>90</sup> (eq. 1.15). Possibly, some direct Ta...C( $\delta$ ) interaction is more easily attainable in this geometry.

eq. 1.15



The critical effect of the substituents on the conformation of the metallacyclic ring is clearly demonstrated by the two

isomeric 1,4-dicyanocobaltacyclopentanes (1.33) and (1.34).<sup>91</sup> The cobaltacyclopentane ring in the cis form is an opened-envelope conformation while that of the trans isomer is puckered.



(1.33)



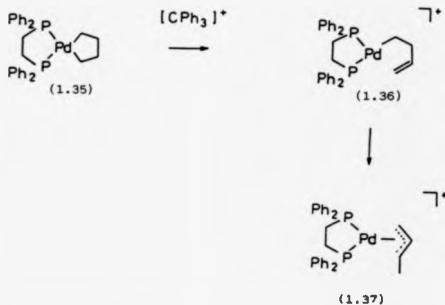
(1.34)

## 1.5 REACTIONS OF METALLACYCLOALKANES

### 1.5.1 Interconversion of Metal $\pi$ -allyls and Metallocycloalkanes

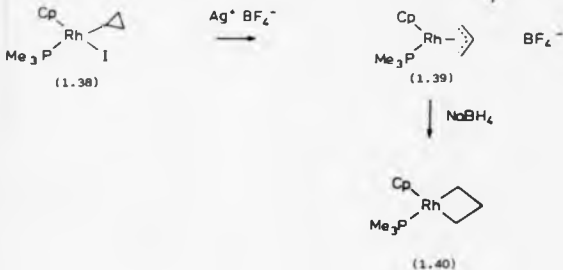
An interesting reaction which interrelates two important classes of organometallic compounds is the  $\pi$ -allyl metal hydride - metallocycloalkane transformation.<sup>100</sup> In the course of their studies on the preparation and reactivity of palladacyclopentanes Ingrosso *et al.*<sup>27,101</sup> found that palladacyclopentanes (1.35) undergo a facile hydrogen abstraction by the trityl cation to give an intermediate (1.36) which rearranges to give the more stable cationic  $\pi$ -allyl derivative of palladium(II) (1.37) (eq. 1.16).

eq. 1.16



This reaction is reversible and several metallacyclo-butanes and -pentanes have been synthesised by treatment of the corresponding metal-allyl complex with hydride reagents.<sup>38,102-105</sup>

For example, treatment of iodocyclopropylrhodium complex (1.38) with silver fluoroborate gives the corresponding  $\pi$ -allyl complex (1.39). Treatment of (1.39) with  $\text{NaBH}_4$  converts it into the metallacyclobutane (1.40) (Scheme 1.4).<sup>37</sup>



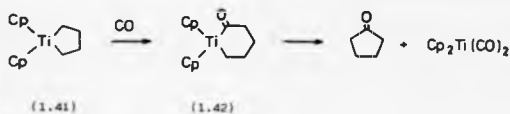
**Scheme 1.4.** Formation of a metallocyclobutane by treatment of a metal  $\eta$ -allyl with a hydride reagent.

Deuterium labelling studies have shown that the addition of the hydride is completely regioselective as well as stereospecific, the hydride adding to the  $\beta$ -carbon syn to the pentamethylcyclopentadienyl ligand.<sup>37</sup>

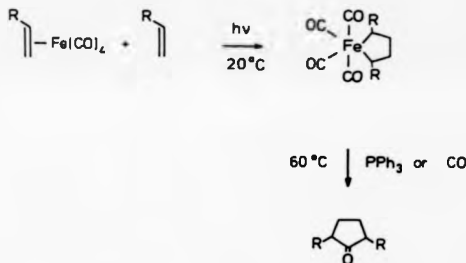
### 1.5.2 Cyclopentanone Synthesis

Several metallacyclopentanes <sup>15,16,19,27,30,79,83,106-108</sup> are known to produce cyclopentanone on reaction with CO (e.g. eq. 1.17). The reaction proceeds by insertion of CO into the metal-carbon bond of the metallacyclopentane (1.41) to form (1.42), followed by reductive elimination of cyclopentanone.<sup>11</sup>

eq. 1.17



The bis-alkene complex-metallacyclopentane transformation is an increasingly important link between diverse classes of organic compounds. For example, the cyclopentanone can be formed from two alkenes, by a sequence involving coupling of the two alkenes into a metallacyclopentane<sup>109</sup> (Scheme 1.5), followed by insertion of CO and reductive elimination of the cyclic ketone.

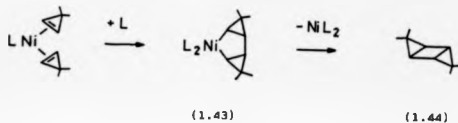


**Scheme 1.5.** Formation of cyclopentanone from alkenes, by a sequence involving coupling of two alkenes forming a metallacyclopentane.

### 1.5.3 Cyclodimerisation of Alkenes

Metallacyclopentanes are intermediates in a number of metal catalysed [2+2] cycloaddition reactions.<sup>7,8,110</sup> Cyclodimers from simple unstrained unsaturated hydrocarbons have been reported to form via nickelacyclopentanes.<sup>49</sup> Singer *et al.*<sup>8,51-54,112</sup> have systematically investigated the cyclodimerisation of strained alkenes such as methylenecyclopropane or dimethylcyclopropanes. In the example shown (eq. 1.18) the product (1.44) results from reductive elimination from the intermediate nickelacyclopentane ring (1.43).

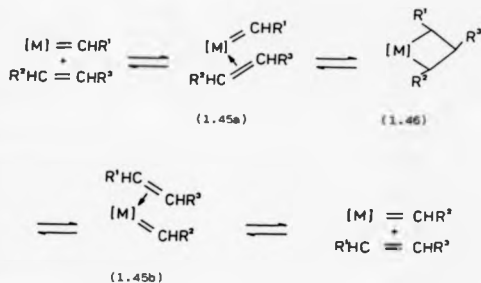
eq. 1.18



### 1.5.4 Alkene Metathesis

Metallacyclobutanes are well established intermediates in alkene metathesis<sup>3,55,83,113-121</sup> in which interconversion of alkene-carbene complex intermediates (1.45a) and (1.45b) with a metallacyclobutane (1.46) takes place (Scheme 1.6).



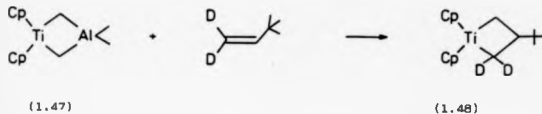


Scheme 1.6. Interconversion of alkene-carbene complexes with metallacyclobutanes.

Grubbs et al.<sup>116,117</sup> have investigated the kinetics and stereochemistry of the titanacyclobutane-titanium methylene interconversion.

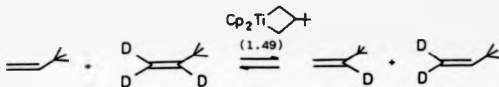
The titanacyclobutane (1.48) synthesised from the well defined metathesis catalyst (1.47) (eq. 1.19) undergoes the reactions expected of a metathesis intermediate.<sup>116</sup>

eq. 1.19



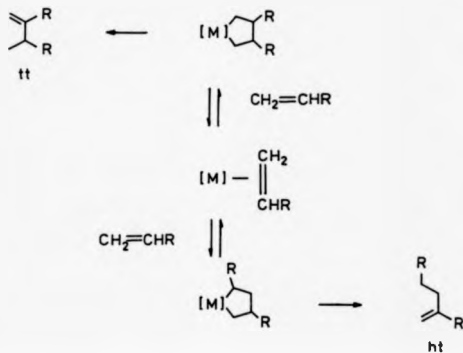
Compound (1.49) catalyses the degenerate metathesis of 3,3-dimethyl-1-butene and 3,3-dimethyl-1-butene-1,1,2-d<sub>3</sub> (eq. 1.20). This is the first example of a metathesis reaction catalysed by a metallacyclobutane alone without the addition of a cocatalyst.<sup>116</sup>

eq. 1.20



### 1.5.5 Alkene Dimerisation

Tantalacyclopentanes have been shown to be active intermediates in the catalytic dimerisation of alkenes to a mixture of tail to tail (tt) dimers and head to tail (ht) dimers.<sup>122-128</sup> Deuterium-labelling studies have shown that each tantalacyclopentane undergoes ring contraction to a tantalacyclobutane ring,<sup>128</sup> initiated by  $\beta$ -hydrogen transfer (see Section 1.5.6), the ring then decomposes selectively to the tt or ht dimers (Scheme 1.7).



Scheme 1.7. Metallacyclopentanes are active intermediates in the catalytic dimerisation of alkenes.

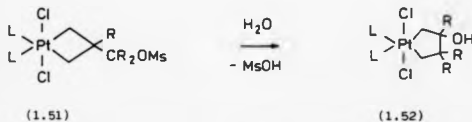
#### 1.5.6 Ring Expansion and Ring Contraction

By analogy to solvolysis of cyclopropylmethyl esters (1.50) which occurs with partial rearrangement to cyclobutyl derivatives<sup>129</sup> (eq. 1.21), the platinacyclobutane (1.51) undergoes solvolysis with ring expansion to the platinacyclopentane (1.52)<sup>130</sup> (eq. 1.22).

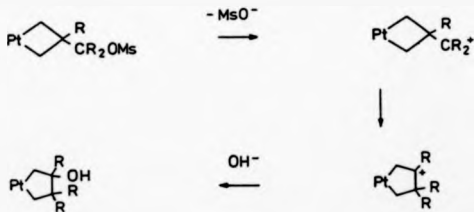
eq. 1.21



eq. 1.22

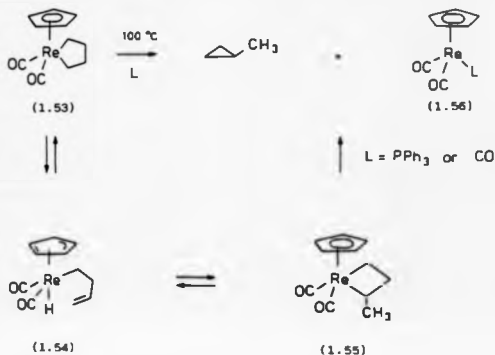


Deuterium labelling studies have indicated that skeletal isomerisation of platinumacyclobutane to platinumacyclopentane occurs prior to hydrolysis (Scheme 1.8).



**Scheme 1.8.** Proposed mechanism of ring expansion of a platinumacyclobutane to a platinumacyclopentane during hydrolysis.

The rhenacyclopentane complex (1.53) upon thermolysis at 100°C undergoes ring contraction to form rhenacyclobutane (1.55) via intermediate (1.54) and then treatment with CO or  $\text{PR}_3$  gives methylcyclopropane and  $[\text{CpRe}(\text{CO})_2\text{PR}_3]$  (1.56)<sup>32</sup> (Scheme 1.9).



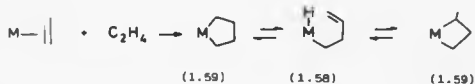
**Scheme 1.9.** Decomposition of a rhenacyclopentane to give methylcyclopropane occurs via ring contraction to a rhenacyclobutane.

Deuterium labelling studies demonstrated that methylcyclopropane formation proceeds by net  $\beta$ - to  $\alpha$ -hydrogen migration, followed by formation of a bond between the  $\beta$ - and the other  $\alpha$ - carbon.

A  $\pi$ - $\pi$  cyclopentadienyl ring slip occurs to generate the vacant coordination site.<sup>131</sup>

Schrock *et al.*<sup>128</sup> proposed that short lived titanacyclobutane intermediates (1.59) are formed from titanacyclopentanes (1.57) during some catalytic alkene dimerisation reactions (eq. 1.23).

eq. 1.23



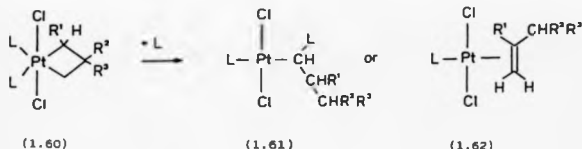
The reverse reaction which should be thermodynamically favoured has not been observed. Deuterium labelling studies<sup>128</sup> have shown that all tantalacyclopentane complexes that decompose to give products of an apparent  $\beta$ -elimination sequence, decompose via metallacyclobutane intermediates.

#### 1.5.7 Decomposition of Platinacyclobutanes to Give Alkene or Ylide Complexes

In a recent report<sup>132</sup> a mechanism has been proposed for the decomposition of platinum(IV) derivatives of metallacyclobutanes which involves an  $\alpha$ -elimination reaction. Previously there were precedents for  $\alpha$ -elimination only in tantalum<sup>128,133</sup> and tungsten<sup>134</sup> compounds although there is recent evidence for  $\alpha$ -elimination in iridium compounds.<sup>135</sup>

Platinacyclobutanes of the type (1.60) decompose on treatment with bulky pyridine derivatives to either the ylide (1.61) or alkene (1.62) (eq. 1.24).

eq. 1.24



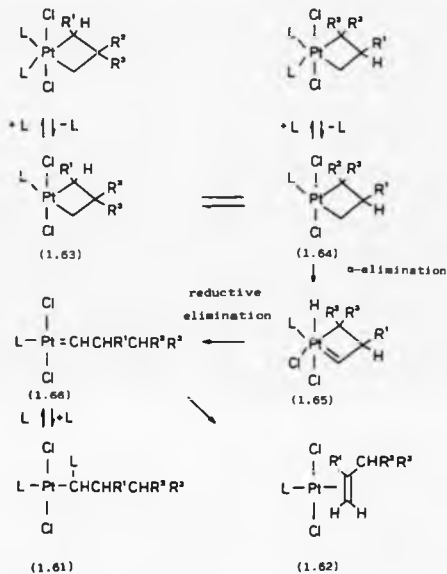
The reactions typically involve skeletal isomerisation (see Section 1.5.8) of the platinacyclobutane at a rate faster than the decomposition to alkene or ylide.

The proposed mechanism is shown in Scheme 1.10. Initial loss of ligand to form (1.63) is followed by skeletal isomerisation to the five coordinate platinacyclobutane (1.64). An  $\alpha$ -elimination to give (1.65) then occurs. Reductive elimination gives the carbene complex (1.66) which can be trapped as the ylide (1.61) or the alkene complex (1.62).

Deuterium labelling studies have shown that decomposition of platinum(IV) derivatives of metallacyclobutanes cannot occur by  $\beta$ -elimination as proposed by Cushman *et al.*<sup>136</sup> and in all cases the results were consistent with  $\alpha$ -elimination occurring from the  $\text{CH}_2$  group of the ring and the hydride being transferred to the most highly substituted carbon of the platinacyclobutane.

#### 1.5.8 Metallacyclobutane Rearrangement

In the course of their studies of the chemistry of platinacyclobutanes, Puddephatt, Tipper<sup>137</sup> and coworkers discovered that platinacyclobutanes (1.67) undergo a rearrangement,



Scheme 1.10. The  $\alpha$ -elimination mechanism for the decomposition of a platinacyclobutane to give an ylide or alkene.



whereby a substituent at the carbon  $\alpha$  to the metal appears to migrate to a  $\beta$ -position (1.68) (eq. 1.25).

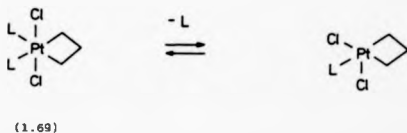
eq. 1.25



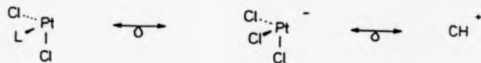
The rearrangement is a skeletal rearrangement rather than a substituent migration.<sup>138</sup> The rearrangement is stereospecific<sup>139</sup> retaining the stereochemistry of the metallacycle and does not involve reductive elimination of cyclopropane.

Several mechanisms have been proposed to explain the available data. Hoffmann *et al.*<sup>140</sup> have proposed a mechanism for the isomerisation which involves using the isolobal analogy. It is known that the first step of the rearrangement involves loss of ligand (eq. 1.26).

eq. 1.26



Hoffmann et al.<sup>140</sup> consider the  $\text{LCl}_2\text{Pt}$  unit in  $[\text{L}_2\text{Cl}_2\text{Pt}(\text{C}_3\text{H}_6)]$  (1.69) to have a pyramidal geometry which is isolobal to  $\text{CH}^+$ .



Thus, the metallocyclobutane  $[\text{LCl}_2\text{Pt}(\text{C}_3\text{H}_6)]$  is isolobal to  $\text{C}_4\text{H}_7^+$ , a non classical carbonium ion.



Hoffmann elegantly shows how the topographies of the potential energy surfaces of the organic and organometallic species are similar indicating that the isolobal inorganic complex should exhibit a pattern of rearrangements similar to those of  $\text{C}_4\text{H}_7^+$ .

## 1.6 METALLACYCLOALKENES

In recent years the importance of unsaturated transition metallacycles in a number of stoichiometric and catalytic reactions has become apparent. There has been extensive research to investi-

gate the chemistry of metallacyclobutenes (1.70), metallacyclobutadienes (1.71), metallacyclopentenes (1.72) and metallacyclopentadienes (1.73). Metallacyclobutenes and metallacyclobutadienes are intermediates in the alkene<sup>141</sup> and in alkyne metathesis,<sup>142-144</sup> respectively. Metallacyclopentenes have been implicated in a number of co-oligomerisation reactions of alkenes with alkynes<sup>145</sup> and metallacyclopentadienes are known to be intermediates in cyclootrimerisation of alkynes to benzenoid compounds<sup>146,147</sup>. In contrast the chemistry of six membered unsaturated metallacycles has remained relatively unexplored.



(1.70)



(1.71)



(1.72)

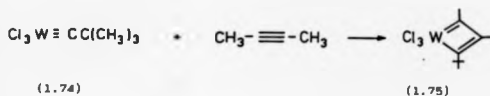


(1.73)

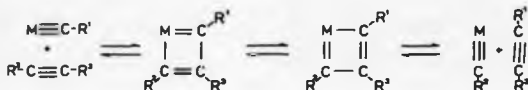
#### 1.7 SYNTHESIS AND REACTIONS OF METALLACYCLOBUTENES AND METALLACYCLOBUTADIENES

A general approach to metallacyclobutadienes is the reaction of metal-carbyne complexes with alkynes. For example, the tungstenacyclobutadiene (1.75) can be made by treatment of the metal-carbyne complex (1.74) with but-2-yne (eq. 1.27).<sup>142</sup>

eq. 1.27



Schrock *et al.*<sup>143,144</sup> have shown that tungstenacyclobutadienes are intermediates in the metathesis of alkynes (Scheme 1.11).



Scheme 1.11. Interconversion of alkyne-carbyne complexes with metallacyclobutadienes.

Metallacyclobutenes (1.76) can also be made in the analogous reaction of metal-carbene complexes with alkynes (eq. 1.28). Katz *et al.*<sup>148</sup> have investigated the metal catalysed rearrangement of alkene-alkynes and the stereochemistry of the metallacyclobutene ring opening.

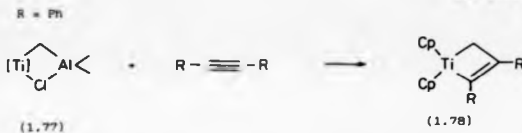
eq. 1.28



(1.76)

The titanacyclobutene (1.78) has been shown to be a transient intermediate in the alkene metathesis reaction.<sup>141</sup> It has been isolated by reaction of the alkene metathesis catalyst (1.77) with an alkyne (eq. 1.29).

eq. 1.29

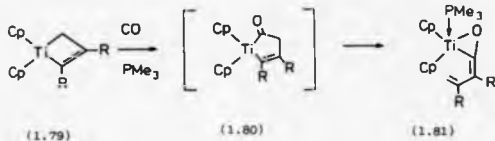


(1.77)

(1.78)

Metallacyclobutenes can also undergo insertion of small molecules into one of the metal carbon bonds. For example carbonylations of titanocene cyclobutenes (1.79)<sup>149</sup> yield titanocenevinyl ketene complexes (1.81) involving the titanocene-acyl complex as an intermediate (1.80) (eq. 1.30).

eq. 1.30



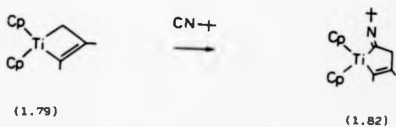
The cyclic ketone 2,3-dimethylcyclopent-2-enone is obtained on carbonylation of the larger titanocene cyclopentene (eq. 1.31).<sup>150</sup>

eq. 1.31



Similarly, treatment of (1.79) with one equivalent of tert-butyl isocyanide gives the imino-acyl complex (1.82) in quantitative yield<sup>149</sup> (eq. 1.32).

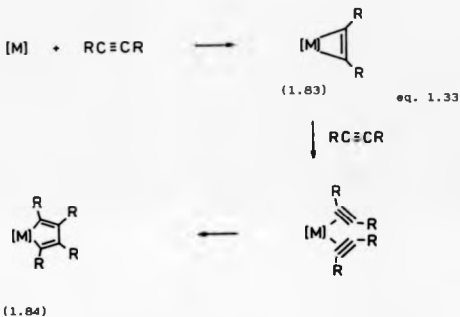
eq. 1.32



## 1.8 SYNTHESIS OF METALLACYCLOPENTENES AND METALLACYCLOPENTADIENES

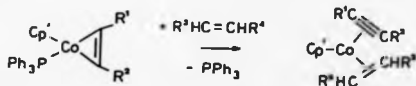
Metallacyclopentadienes of transition metals such as titanium,<sup>151,152</sup> zirconium,<sup>153,155</sup> hafnium,<sup>155</sup> cobalt,<sup>156-158</sup> nickel<sup>159</sup> and palladium<sup>160</sup> have been reported.

The coupling of two alkynes in the coordination sphere of a metal to form metallacyclopentadienes (1.84) is the most common route to these compounds (eq. 1.33).<sup>151-162</sup> A metallacyclopropene (1.83) is an intermediate.

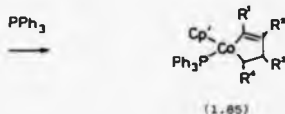


The regioselectivity of the cyclisation process is controlled by two factors, steric and electronic. When the substituents are bulky, the steric factor controls the selectivity.

Metallacyclopentenes (1.85) are produced by a similar reaction involving coupling of an alkene and alkyne at the metal centre.<sup>163</sup> (eq. 1.34).

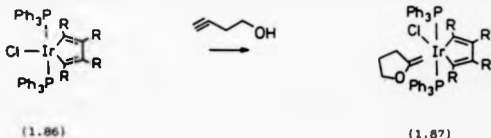


eq. 1.34



Recently,<sup>164</sup> the first isolable metallacyclobutene complex (1.87) has been prepared, in which two important classes of compounds have been combined in a single mononuclear complex. Treatment of the iridacyclopentadiene (1.86) with but-3-ynol gives the neutral complex (1.87) (eq. 1.35).

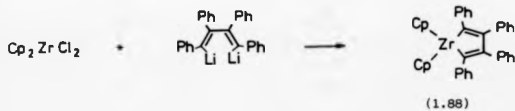
eq. 1.35



Metallacyclopentadienes can also be synthesized by reaction of the metal dihalide with the appropriate 1,4-dilithiobutadiene. For example, one of the earliest examples of such a reaction is the treatment of  $[\text{Cp}_2\text{ZrCl}_2]$  with 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (eq. 1.36) to give the zirconacyclopentadiene (1.88).<sup>165</sup>

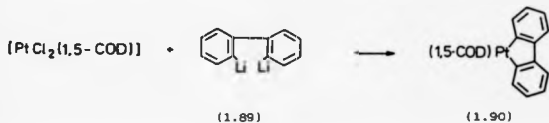


eq. 1.36

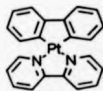


Another common route to compounds containing the metallocyclopentadiene moiety (1.90) is reaction of 2,2-dilithiobiphenyl (1.89) with the metal dihalide<sup>165-169</sup> (eq. 1.37).<sup>169</sup>

eq. 1.37



Recently, compounds such as (1.91) which contain the metallocyclopentadiene moiety have been prepared.<sup>170</sup>



(1.91)

## 1.9 REACTIONS OF METALLACYCLOPENTENES AND METALLACYCLOPENTADIENES

### 1.9.1 Cyclisation Reactions

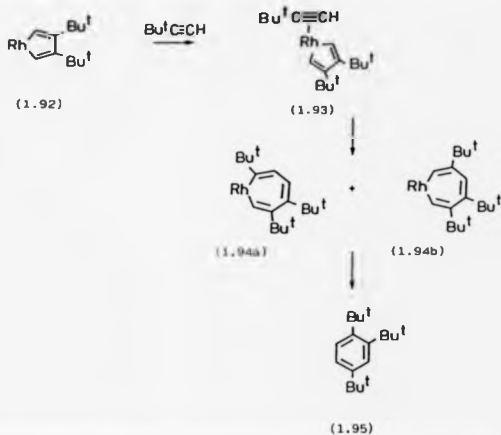
Metallacyclopentenes and metallacyclopentadienes play important roles in transition-metal promoted reactions of unsaturated hydrocarbons.

#### 1.9.1.1 Cyclotrimerisation of Alkynes

Metallacyclopentadiene complexes are believed to be important intermediates in the transition metal catalysed cyclo-trimerisation of alkynes.<sup>171</sup> Cobalt-,<sup>172,142</sup> rhoda-,<sup>143</sup> and pallada-,<sup>174</sup> cyclopentadienes have been treated with acetylenes to give benzene derivatives (e.g. Scheme 1.12).

The reaction involves insertion of the coordinated alkyne into the metal-carbon  $\sigma$  bond of the metallacyclopentadiene ring in compound (1.93) leading to metallacycloheptatrienes (1.94a) and (1.94b). The final step is reductive elimination of the benzene derivative (1.95) with release of the coordinatively unsaturated metal fragment.

Metallacyclopentadienes are intermediates in the reaction of two alkynes with an alkene leading to the formation of cyclohexadienes.<sup>166</sup> Metallacyclopentenes have been implicated in a number of reactions of alkenes with alkynes catalysed by cobalt,<sup>141,146</sup> rhodium<sup>147</sup> and molybdenum.<sup>175</sup>



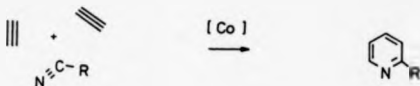
**Scheme 1.12.** Cyclotrimerisation of Alkynes involving metallocyclopentadiene as an intermediate.

#### 1.9.1.2 Pyridine Synthesis from Alkynes and Nitriles

A cobaltacyclopentadiene (1.96) is a known intermediate in the well defined cobalt-catalysed pyridine synthesis from alkynes and nitriles.<sup>13,14</sup> Pyridines are technically important fine chemicals and can be made selectively and in one step from ethyne

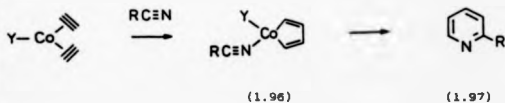
and the appropriate nitrile compound using soluble organocobalt catalysts [Co] (eq. 1.38).

eq. 1.38



The catalytic reaction involves coupling of the two alkynes at the cobalt centre to form a metallocyclopentadiene (1.96) followed by insertion of the nitrile into the metal-carbon  $\sigma$ -bond and reductive elimination of the substituted pyridine (1.97) (e.g. eq. 1.39).

eq. 1.39



Fehlner et al.<sup>176</sup> have synthesised a metallocarborane by a method in which a metallacyclopentadiene is used as the metal-carbon source. Reaction of the cobaltacyclopentadiene (1.98) with  $\text{BH}_3$ ·THF produces the nido cobaltacarborane (1.99) in 20% yield (eq. 1.40).

eq. 1.40

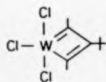


The significance of this work lies in the demonstration that metallacycles provide a viable route to metallacarboranes. Considering the variety in the type of metallacycles known, this particular method may lead to some unusual compounds.

## 1.10 X-RAY CRYSTAL STRUCTURES OF METALLACYCLOBUTENES, METALLACYCLOBUTADIENES AND METALLACYCLOPENTADIENES

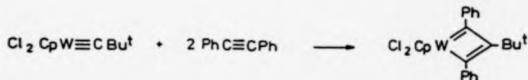
The reported crystal structures of metallacyclobutadienes 142-144,177-180 show that the ring either adopts a planar conformation containing delocalised bonds or a non planar conformation containing localised single and double bonds. 182

Many of the metallacyclobutadiene rings are planar and delocalised.<sup>142,143,178</sup> For example the  $WC_3$  ring system in compound (1.100) is planar.<sup>178</sup>



(1.100)

In contrast to compound (1.100) the  $WC_3$  ring in the tungsten-acyclobutadiene (1.102) made by treatment of  $[Cl_2CpWC Bu^t]$  (1.101) with diphenylacetylene (eq. 1.41), is found to be severely puckered with localised single and double carbon-carbon bonds.<sup>180</sup>



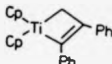
(1.101)

(1.102)

It is interesting to note that the  $WC_3$  carbons have scrambled and the two phenyl groups are no longer on adjacent carbon atoms. The rearrangement is thought to involve the formation of a tungsten(VI) metallatetrahedrane.

It is not clear if the deviation from planarity in (1.102) is a result of steric requirements of the bulky cyclopentadienyl ligand vis a vis the chloride ligand or whether it is a change necessary to accommodate the more bulky substituents.

The ring in titanacyclobutene (1.103) is found to be planar with a localised carbon-carbon double bond.<sup>181</sup>

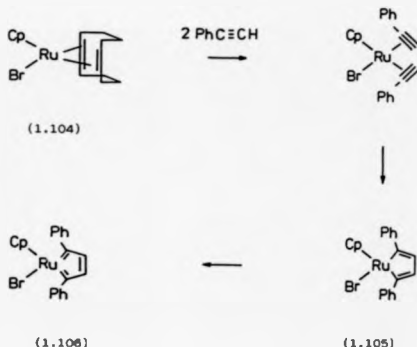


(1.103)

The crystal structures of metallacyclopentadienes for a wide range of metals show the rings to be essentially planar with localised single and double bonds. Hoffmann *et al.*<sup>182</sup> have investigated theoretically the absence of delocalisation of electrons in these compounds. In several titana-,<sup>151</sup> hafna-,<sup>155</sup> cobalta-,<sup>156</sup> rhoda-,<sup>156</sup> and palladacyclopentadienes<sup>160</sup> the bond length sequence short/long/short varies between 1.33 and 1.38 Å on one side to 1.39 and 1.51 Å on the other.

#### 1.11 SYNTHESIS AND STRUCTURE OF METALLACYCLOPENTATRIENES

The first example of a metallacyclopentatriene has been recently reported.<sup>183</sup> Cyclodimerisation of two molecules of phenyl-acetylene at the ruthenium(II) centre in  $[(\eta-C_5H_5)Ru(\eta-C_8H_{12})Br]$  (1.104) does not yield the expected metallacyclopentadiene (1.105) (see Section 1.8) but the metallacyclopentatriene (1.106) (Scheme 1.13).



Scheme 1.13. Formation of a metallacyclopentatriene by coupling of two alkynes at an unsaturated metal centre.

The X-ray crystal structure of (1.106) shows that the phenyltriene substituents are in the  $\alpha$ -positions. The ruthenacyclopentatriene ring is close to planar with the ruthenium atom lying only 0.215 Å out of the  $\text{C}_4$  plane.

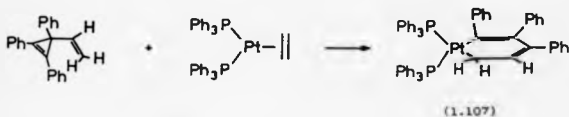
The formation of a metallacyclopentatriene rather than the expected metallacyclopentadiene is thought to be due to the unsaturation at the ruthenium centre. This is shown by the facile oxidative addition of the metallacyclopentatriene (1.106) with donor ligands such as dimethylphenylphosphine to give the ruthenacyclopentadiene  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_2\text{Ph})(\text{C}_4\text{H}_2\text{H}_2)\text{Br}]$ .



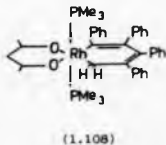
## 1.12 SYNTHESIS AND STRUCTURE OF METALLACYCLOHEXADIENES

Until 1986, no examples of unsaturated six membered platinacycles were known. The first example of a compound containing a 1-metallacyclohexa-2,4-diene ring (1.107) was reported in 1986 by Hughes *et al.*<sup>184</sup> Complex (1.107) was made from 1,2,3-triphenyl-3-vinylcycloprop-1-ene and the 16 electron complex  $[\text{Pt}(\text{n}^1\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$  (eq. 1.42).

eq. 1.42



Hughes *et al.*<sup>185</sup> have also synthesised the air stable 1-rhodacyclohexa-2,4-diene complex (1.108).

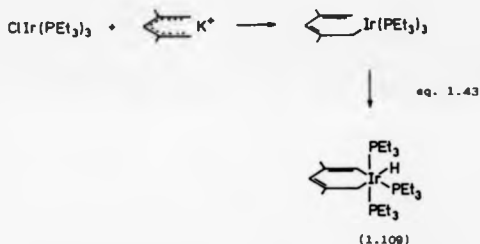


The X-ray crystal structures of complexes (1.107) and (1.108) show that the metallacyclic ring contains localised single and double bonds between the carbon atoms. In both compounds the metallacyclic ring is puckered, although the ring in the octahedral

compound (1.108) is less puckered. The flattening of the ring in (1.108) is probably a result of the presence of  $\text{Ph}_3\text{P}$  above and below the ring.

This flattening of the ring in (1.108) is also observed in solution where low temperature n.m.r. studies of (1.108) indicate that even at  $-96^\circ\text{C}$  the  $\text{CH}_2$  protons are either equivalent or the ring is undergoing rapid ring reversal. In contrast, n.m.r. studies of (1.107) show that the  $\text{CH}_2$  protons in the ring are inequivalent at room temperature.

Recently Bleeker *et al.*<sup>186</sup> have synthesised an iridacyclohexadiene (1.109) by treatment of  $[\text{ClIr}(\text{PET}_3)_3]$  with potassium 2,4-dimethylpentadienide (eq. 1.43).

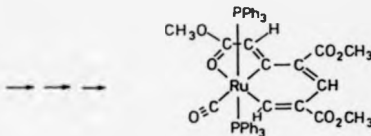
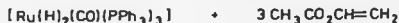


The X-ray crystal structure of (1.109) again shows the presence of localised single and double bonds in the ring. However the metallacyclic ring in (1.109) is almost planar; none of the atoms deviate by more than  $0.015 \text{ \AA}$  from the plane. N.m.r. studies demonstrate that the planarity of the metallacyclic ring is maintained in solution. The puckering of the ring in compounds

(1.107) and (1.108) may arise from the need to minimise steric contacts between the phenyl substituents on the ring carbons.

A ruthenium metallacyclohexadiene (1.110) has been prepared by reaction of  $[\text{Ru}(\text{H})_2(\text{CO})(\text{PPh}_3)_3]$  with methylpropiolate (eq. 1.44). The reaction involves several steps and the resulting metallacycle consists of three methylpropiolate molecules and a ruthenium.<sup>187</sup>

eq. 1.44



(1.110)

A molybdenum metallacyclohexadiene has been reported to be a possible intermediate in the formation of  $\eta^4$ -cyclopentadiene-molybdenum complexes.<sup>188</sup>

### 1.13 SYNTHESIS AND STRUCTURE OF METALLACYCLOHEXATRIENES

Metallacyclohexatrienes are an interesting class of compounds because there is the possibility of delocalisation over the six atoms of the ring to give an aromatic metallabenzene. Precedents for this occurring are known in main group chemistry. Replacement

of a CH group in benzene by N, P or As leads to stable aromatic molecules such as pyridine, phosphabenzene<sup>189,190</sup> and arsa-benzene.<sup>191,192</sup> Replacement of CH by the isoelectronic O<sup>+</sup> leads to the formation of the pyrylium anion<sup>193</sup> while replacement by B<sup>-</sup>Ph leads to the formation of 1-phenylborabenzene anion.<sup>194</sup>

Replacement of a CH group in benzene by a transition metal together with its associated ligands and the theoretical possibility of electron delocalisation in the resulting ring has been considered by Thorn and Hoffmann.<sup>182</sup> Such a system (1.111) is a metallacyclohexatriene or "metallabenzene".



(1.111)

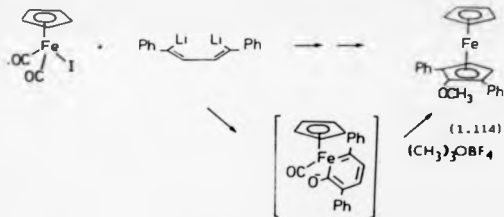
Only one metallabenzene [Os(CSCHCHCHCH)CO(PPh<sub>3</sub>)<sub>2</sub>] (1.112) has previously been reported in the literature.<sup>195</sup> The X-ray crystal structure shows the six membered ring is planar with no significant alternation of carbon-carbon bond lengths, thus supporting the idea of electron delocalisation within the ring.



(1.112)

Allison *et al.*<sup>196</sup> attempted to prepare a metallacyclohexatriene moiety by treating  $[(C_5H_5)Fe(CO)_2I]$  with (E,E)-1,4-dilithio-1,4-diphenylbutadiene with the assumption that concomitant formation of metal-acyl and metal-carbene bonds would occur. Complex (1.114) was formed (eq. 1.45). However it was proposed that the ferrabenzene complex (1.113) was a plausible intermediate.

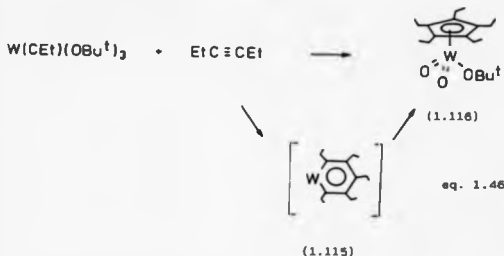
eq. 1.45



(1.113)

Schrock *et al.*<sup>144,197</sup> (1.112) have found that  $[W(CET)(OBu^t)_3]$  reacts with hex-3-yne to give a pentaethylocyclopentadienyl ligand

(1.116) (eq. 1.46). In this case a metallacyclohexatriene (1.115) is a possible intermediate.



#### 1.14 AIMS OF THE PRESENT WORK

In contrast to the very considerable amount of research carried out on metallacyclopentanes and metallacyclobutanes, metallacyclohexanes remain relatively unexplored. No X-ray crystal structure of a metallacyclohexane has been reported.

In view of the rich conformational properties of cyclohexane and other six membered rings we thought it would be interesting to synthesise a series of platinacyclohexanes and determine how the metal and substituents on the ring affect the conformation.

Similarly, metallacyclohexadienes and especially metallacyclohexatrienes remain unexplored in comparison to the smaller size metallacycloalkenes. The chemistry of compounds containing the platinacyclohexadiene moiety and the possibility of obtaining a platinacyclohexatriene or 'platinabenzene' moiety were investigated.

CHAPTER TWO  
SYNTHESIS, CHARACTERISATION AND CONFORMATIONAL STUDIES  
OF SATURATED AND UNSATURATED SIX MEMBERED PLATINACYCLES

2.1 CONFORMATIONAL STUDIES OF SATURATED AND UNSATURATED SIX  
MEMBERED HETEROCYCLES

2.1.1 Saturated Six Membered Heterocycles

Conformational analysis of six membered heterocycles is a topic of wide interest.<sup>198-204</sup> The replacement of a single methylene unit in cyclohexane by a heteroatom and its associated substituents or lone pairs provides rings with a rich variety of conformational properties. The conformational studies that have been reported have been concerned with heterocycles containing main group elements.<sup>205-211</sup>

The most common conformation adopted by cyclohexane<sup>212,213</sup> and saturated six membered heterocycles is the chair (Fig. 2.1) in which all the bonds are staggered.

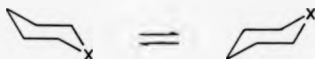


Fig. 2.1. Chair conformation of cyclohexane.

The torsional arrangements of the ring atoms in cyclohexane are altered when a methylene unit is replaced with a heteroatom. As a result, the ring may be more flattened or puckered than cyclohexane. In some cases certain portions of the ring are flattened while others within the ring are puckered.<sup>199</sup>

Chair conformations undergo ring reversal, often rapidly on the n.m.r. timescale at ambient temperatures (eq. 2.1).<sup>213</sup>

eq. 2.1



This fluxionality has been studied by variable temperature <sup>1</sup>H n.m.r. spectroscopy for many heterocycles<sup>214</sup> and from n.m.r. lineshape analysis the kinetic parameters for the process have been determined.<sup>215</sup> Generally the free energy of activation  $\Delta G^\ddagger$  falls in the range 25-60 kJ mol<sup>-1</sup>,<sup>198</sup> the precise value depending on the heteroatom and the nature of the substituents on the ring.

Any process equilibrating two equivalent chair forms involves rotation about certain bonds. Therefore the barrier to ring reversal will be dependent on the barriers to torsion about these bonds. If the C-X torsional barrier is considerably different from the C-C torsional barrier, then the ring reversal in the six membered heterocycle can be expected to be different from that of cyclohexane.<sup>201</sup>



Replacement of a methylene unit in cyclohexane by other Group IV (group 14) elements and their substituents causes the barrier to ring reversal of the resulting chair conformation to be lowered. For example the ring reversal of 1,1-dimethylsilacyclohexane (2.1b) has been studied by low temperature n.m.r. methods and has a lower barrier ( $\Delta G^\ddagger = 23.0 \text{ kJ mol}^{-1}$ )<sup>211</sup> than cyclohexane (2.1a) ( $\Delta G^\ddagger = 43.1 \text{ kJ mol}^{-1}$ ).<sup>216</sup> Few conformational studies have been reported for the other six membered rings containing Group IV heteroatoms. Germa- (2.1c),<sup>217</sup> stanna- (2.1e)<sup>218</sup> and plumba- (2.1f)<sup>218</sup> cyclohexanes are known and by analogy with silacyclohexane, the barrier to ring reversal should be low, but these have not been reported. The proton spectrum of 1,1-dimethylgermacyclohexane (2.1d) remained unchanged down to  $-130^\circ\text{C}$  at a field corresponding to 270 MHz.<sup>217</sup>



- |        |         |                     |
|--------|---------|---------------------|
| (2.1a) | X = C,  | R = H               |
| (2.1b) | X = Si, | R = CH <sub>3</sub> |
| (2.1c) | X = Ge, | R = H               |
| (2.1d) | X = Ge, | R = CH <sub>3</sub> |
| (2.1e) | X = Sn, | R = H               |
| (2.1f) | X = Pb, | R = H               |

For the group V (group 15) heterocycles the free energy of activation  $\Delta G^\ddagger$  for ring reversals are in the general order  $N > P > As$ . Most of the conformational studies have been concerned with piperidine (2.2a) and its derivatives.<sup>219-226</sup> Piperidines substituted at nitrogen only, are all found to adopt chair conformations.



(2.2a) X = N, R = H

(2.2b) X = N, R = CH<sub>3</sub>

(2.2c) X = P, R = H

(2.2d) X = As, R = CH<sub>3</sub>

(2.2e) X = Sb, R = H

(2.2f) X = Bi, R = H

The ring in piperidine itself and its N-methyl derivative (2.2b) is essentially undistorted from the shape of the cyclohexane chair, despite the slightly different C-N bond length and C-N-C bond angle. The barriers to ring reversal of both piperidine ( $\Delta G^\ddagger = 43.5 \text{ kJ mol}^{-1}$ ) and its N-methyl derivative ( $\Delta G^\ddagger = 50.2 \text{ kJ mol}^{-1}$ ) are slightly higher than that of cyclohexane.<sup>226</sup>

In the simple phosphorinane (2.2c) the bond angles around the trivalent phosphorus atom have been found to be significantly

less than tetrahedral<sup>227</sup> and therefore it is reasoned that the phosphorus atom has a hybridisation between p and  $sp^1$ . The smaller C-P-C bond angle and longer C-P bonds led to slightly flattened chair conformations compared with cyclohexane. The free energies of activation for ring reversal were found<sup>228,229</sup> to be about  $\Delta G^\ddagger = 35.5 \text{ kJ mol}^{-1}$  for all substituents on phosphorus, significantly lower than those in the analogous piperidines. The barrier to ring reversal of 1-methylarsenane (2.2d) ( $\Delta G^\ddagger = 28.5 \text{ kJ mol}^{-1}$ )<sup>230</sup> is lower than that of the corresponding phosphorinane. Conformational studies of antimonane (2.2e) and bisminane<sup>198</sup> (2.2f) have not been reported.

In the group VI (group 16) heterocycles the free energy of activation  $\Delta G^\ddagger$  for ring reversal decreases on passing down the group, i.e.  $O > S > Se > Te$ . Tetrahydropyran (2.3a) has a chair conformation that is slightly flattened from the shape of cyclohexane.<sup>199</sup> This distortion is a result of the larger C-O-C bond angle and shorter C-O bond length. The barrier to ring reversal ( $\Delta G^\ddagger = 43.1 \text{ kJ mol}^{-1}$ )<sup>231</sup> is very similar to that of cyclohexane.

In thiiane (2.3b), the longer C-S bond and the smaller C-S-C angle cause the thiiane ring to be distinctly puckered with respect to shape of cyclohexane.<sup>200</sup> However, the barrier to ring reversal of thiiane ( $\Delta G^\ddagger = 39.3 \text{ kJ mol}^{-1}$ )<sup>232</sup> is lower than for tetrahydropyran. This is probably due to the lower torsion for the C-S bond ( $8.91 \text{ kJ mol}^{-1}$ ) as compared with the C-O bond ( $10.46 \text{ kJ mol}^{-1}$ ).<sup>208</sup>

The selenium and tellurium heterocycles are similar to thiane in that the rings are also highly puckered.<sup>232</sup> The barrier to ring reversal in selenane (2.3c) ( $\Delta G^\ddagger = 34.7 \text{ kJ mol}^{-1}$ ) is slightly lower than in thiane with the barrier in tellurane (2.3d) ( $\Delta G^\ddagger = 30.5 \text{ kJ mol}^{-1}$ ) even lower. It would appear that angle bending is much less important than the bond torsion in determining the barrier to ring reversal, since the barrier to ring reversal becomes lower as the degree of puckering increases.<sup>232</sup> The decrease in the energy barriers are related to similar decreases observed in the C-X torsion.



(2.3a) X = O

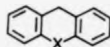
(2.3b) X = S

(2.3c) X = Se

(2.3d) X = Te

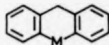
### 2.1.2 Unmaturated Six Membered Heterocycles

One class of compounds which contain six membered heterocycles are 9,10-dihydroheteroanthracenes (2.4).<sup>233-237</sup>



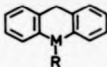
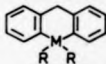
(2.4)

The heteroatom in the many examples of these compounds reported (2.5a) - (2.7d)<sup>238-248</sup> are main group elements.



(2.5a) M = O

(2.5b) M = S

(2.6a) M = P, R = CH<sub>3</sub>(2.6b) M = As, R = CH<sub>3</sub>(2.6c) M = Sb, R = CH<sub>3</sub>

(2.7a) M = C, R = H

(2.7b) M = Si, R = H

(2.7c) M = Si, R = CH<sub>3</sub>(2.7d) M = Sn, R = CH<sub>3</sub>

If such molecules are to be planar, all the internal angles of the heterocyclic ring are required to be 120°. This would be expected to introduce considerable angle strain into the molecule

since the heteroatom at position 9 and the tetravalent carbon atom at position 10 require greatly reduced angles in the range  $90-109^\circ$ , in their coordination geometries. Hence they are folded about the C(10)-X axis and give rise to folded molecules in which the six membered heterocycle adopts a boat conformation (Fig. 2.2).

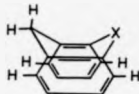


Fig. 2.2. Boat conformation of central ring of 9,10-dihydroanthracenes (X = carbon or heteroatom).

A measure of the degree of folding is given by the dihedral angle of fold,<sup>249</sup> which is the angle between the two planes [C(9), C(10), C(11), C(12)] and [C(9), C(10), C(13), C(14)] (Fig. 2.3). A planar tricyclic molecule would have a dihedral angle of fold of  $180^\circ$ .

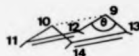


Fig. 2.3. Dihedral angle  $\theta$  between planes [C(9), C(10), C(11), C(12)] and [C(9), C(10), C(14), C(13)].

In 9,10-dihydroanthracene the optimum geometry has been calculated by molecular mechanics<sup>249</sup> to be planar although the energy required for non planar distortion is small. The energy required for 20° distortion from planarity is calculated to be only 1.7 kJ mol<sup>-1</sup>. The thermal energy available at room temperature (RT = 2.5 kJ mol<sup>-1</sup>) and the entropy contribution favouring lower symmetry will result in large puckering amplitudes. The X-ray crystal structure of 9,10-dihydroanthracene indicates that the central ring adopts a boat conformation with a dihedral angle of 145°. <sup>250</sup>

The X ray crystal structures of a number of substituted 9,10-dihydroanthracenes and 9,10-dihydroheteroanthracenes have been determined.<sup>251-258</sup> It is evident that the nature of the heteroatom and the number and type of substituents affect the geometry of the 9,10-dihydroanthracene. The dihedral angle of fold is affected by the presence of the heteroatom, e.g. this angle is reduced from 145° in 9,10-dihydroanthracene (2.7a) to 136° in

9,10-dihydro-9-silaanthracene (2.7b).<sup>253</sup> The number and nature of substituents R (other than hydrogen) on the 9 and 10 positions of the ring also affect the dihedral angle of fold. When the tetravalent carbon atoms at the 9 and 10 positions in 9,10-dihydroanthracene bear substituents, these may occupy pseudo-axial ( $R_{ax}$ ) or pseudo-equatorial ( $R_{eq}$ ) positions (Fig. 2.4).

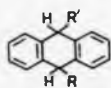


Fig. 2.4. Substituents R on meso positions 9 and 10 may occupy pseudo-axial ( $R_{ax}$ ) or pseudo-equatorial ( $R_{eq}$ ) positions.

The placement of one or two substituents in the pseudo-axial positions results in an increase in the dihedral angle of fold relative to the parent 9,10-dihydroanthracene ( $R = R' = H$ ), i.e. causes flattening of the central ring.<sup>253</sup> whereas a substituent in the pseudo-equatorial position results in a decrease in the angle of fold (Table 2.1).



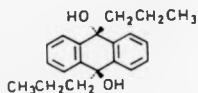
Table 2.1. Dihedral angles of substituted 9,10-dihydroanthracenes.

	R	R'	Dihedral Angle
	H	H	145 <sup>250</sup>
	H	C(CH <sub>3</sub> ) <sub>3</sub> <sup>a</sup>	147 <sup>255</sup>
	CH <sub>3</sub> <sup>a</sup>	C <sub>2</sub> H <sub>5</sub> <sup>a</sup>	152 <sup>256</sup>
	CH <sub>3</sub> <sup>a</sup>	CH(CH <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	129 <sup>257</sup>

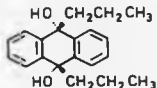
<sup>a</sup> occupy pseudo-axial position

e occupy pseudo-equatorial position

Not only is the degree of substitution an important factor in influencing the geometry of the ring but also the stereochemistry of the substituents. For example, in trans-9,10-dihydro-9,10-dipropyl-anthracene-9,10-diol (2.8) the tricyclic system is essentially planar.<sup>251,259</sup> In a planar configuration the interactions between the peri protons on carbon atoms C(1), C(4), C(5) and C(8) and the 9,10-substituents are minimised. However in the cis-isomer (2.9) the central ring adopts a boat conformation.<sup>251,259</sup>



(2.8)



(2.9)

In solution the boat conformation can undergo ring reversal (eq. 2.2) to its inverted form.<sup>233,260</sup>

eq. 2.2



The transition state for ring reversal is most likely to be planar requiring internal angles in the heterocyclic ring of approximately  $120^\circ$ .<sup>244</sup> The four trigonal carbon atoms of the heterocyclic ring already have the planar geometry for the transition state. Both the heteroatom and tetravalent carbon atom at positions 9 and 10 have to undergo angle deformations to obtain

this planar geometry. Introduction of a heteroatom into the ring will therefore be expected to alter the energy barrier by increased or decreased angle strain effects.

Substituents at either the 9 or 10 position will also affect the barrier,<sup>233</sup> since in the transition state the non bonded interactions between the peri protons on carbon atoms C(1), C(4), C(5) and C(8) and the substituents will be increased (Fig. 2.5).

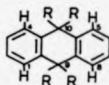


Fig. 2.5. Proposed planar transition state of ring reversal in which R substituents at meso positions 9 and 10 may be subjected to non bonded interactions with the peri protons on C(1), C(4), C(5) and C(8).

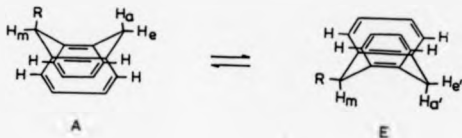
The fluxionality of the ring reversal has been studied by variable temperature  $^1\text{H}$  n.m.r. spectroscopy.<sup>260</sup> The  $^1\text{H}$  n.m.r. spectra of many of the unsubstituted 9,10-dihydroheteroanthracenes and 9,10-dihydroanthracene itself, consists of a singlet for the methylene protons at ambient temperature.<sup>260</sup> This alone does not distinguish between a rapidly inverting system or a static planar one. However 9,10-dihydroanthracene has a dipole moment of 0.4 D in solution<sup>261</sup> and so indicates that the compound is non planar in solution.

The barrier for ring reversal in 9,10-dihydroanthracenes and structurally similar heterocycles is quite low ( $< 30 \text{ kJ mol}^{-1}$ ).<sup>244</sup> and attempts to measure the barrier for ring reversal in 9,10-dihydroanthracene itself have been unsuccessful. The methylene protons are n.m.r. equivalent even at  $-100^\circ\text{C}$  and 100 MHz.<sup>262</sup>

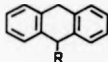
The low energy barrier of 9,10-dihydroanthracene and 9,10-dihydro-9-heteroanthracenes is due to the absence of any atoms (other than hydrogen) bonded to the meso positions, 9 and 10, required to pass by the peri protons to achieve conformational exchange.

In 9,10-dihydroanthracene ( $\text{R}=\text{H}$ ) the two boat conformers are in 1:1 equilibrium (eq. 2.3). However the presence of a substituent R other than hydrogen at the 9 position can alter this equilibrium to favour one of the two conformers.<sup>263</sup> i.e. either A in which R is pseudo-axial or E in which R is pseudo-equatorial (eq. 2.3).

eq. 2.3



Conformational studies of 9-alkyl-9,10-dihydroanthracenes (2.10a-e) have shown that when  $R = Et$ ,  $Bu^t$  or  $Pr$ , the boat exists preferentially, if not exclusively in conformer A where R is pseudo-axial. The 9-methyl (2.10d) and 9-phenyl (2.10e) substituted compounds appear to exist as equilibrium mixtures of the two conformers but with R predominantly in the pseudo-axial position.



(2.10a)  $R=Et$

(2.10b)  $R=Bu^t$

(2.10c)  $R=Pr$

(2.10d)  $R=Me$

(2.10e)  $R=Ph$

In both conformers A and E, it is the pseudo-equatorial groups which undergo the greatest non bonded interactions with the peri protons. Thus to alleviate these interactions, bulky substituents prefer to occupy pseudo-axial positions.

For compounds (2.10a-e) the  $^1\text{H}$  n.m.r. spectrum shows an AB pattern for the methylene protons ( $\text{H}_a$  and  $\text{H}_e$ ) [ $^2J(\text{H}_a, \text{H}_e) = 18 \text{ Hz}$ ], with longer range homoallylic coupling to the meso proton  $\text{H}_m$  at C(9) observed. The spectra for (2.10a-d) are essentially independent of temperature to  $-37^\circ\text{C}$  at 100 MHz.

In contrast to the other alkyl derivatives, the 9-phenyl derivative (2.10e) exhibits equal homoallylic coupling at room temperature but at  $-37^\circ\text{C}$  the two couplings are no longer equal. The barrier to ring inversion is low when  $\text{R}=\text{Ph}$ <sup>263</sup> because the phenyl group can lie parallel to the C(9) and C(10) axis (Fig. 2.6) as the system passes through the transition state, thereby reducing the steric interactions with the peri protons relative to those in the case of  $\text{R} = \text{methyl}$  or a larger group.



Fig. 2.6. Transition state of ring reversal of (2.10e) where phenyl substituent lies parallel to C(9) and C(10) axis.

### 2.1.3 Aims and Scope of the Present Work

The conformational studies reported to date of saturated six membered heterocycles or unsaturated 9,10-dihydrohetero anthracenes have been concerned with p block heteroatoms. These atoms are similar to carbon in two respects. Firstly they use s and p orbitals in their hybridisation and therefore have bond angles in the range  $90-109^\circ$  and secondly the atoms are usually of comparable size. No conformational studies have been reported for either class of heterocycles, where the hetero atom is a transition metal element. It was therefore of interest to determine the effect of replacing a methylene unit in the six membered saturated cyclohexane by platinum(II) (2.11) on the conformation of the ring and the barrier to ring reversal.

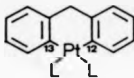


(2.11)

Platinum(II) unlike the heteroatoms previously described, can use s, p and d orbitals in its hybridisation and generally has a square planar geometry requiring an angle of  $90^\circ$ . It is also much larger than a carbon atom (covalent radii, Pt:  $1.31 \text{ \AA}$ ; C(sp<sup>3</sup>):  $0.77 \text{ \AA}$ ).<sup>26a</sup> It is not clear from the previous studies on the main group heterocycles how the smaller C-Pt-C angle and the longer C-Pt bonds (ca  $0.5 \text{ \AA}$  longer than C-C bonds) will affect the conformation of the ring compared to cyclohexane.

Metallacycles containing transition metals are known to be important intermediates in a number of stoichiometric and catalytic reactions.<sup>17,18</sup> A knowledge of the chemical and physical properties of such compounds is important in gaining an understanding of these processes.

Similarly, it would be of interest to determine the effect of replacing the methylene unit at the 9-position in 9,10-dihydroanthracene by platinum(II) and its ligating groups (2.12) on the conformation of the ring. The fact that the platinum has a square planar geometry not only means its bond angles are reduced to 90° but that its coordinated ligands will be in the same plane as the platinum atom and ligated carbon atoms C(12) and C(13).



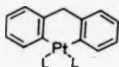
(2.12)

These ligands may be subjected to non bonded interactions with the peri protons on carbon atoms C(1) and C(8) and this may also affect the conformation of the six membered heterocyclic ring.

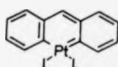
Finally, it would be interesting to compare the effect of a square planar platinum atom on the chair conformation of a six membered saturated ring and the boat conformation of a six membered unsaturated ring.



To date, there have been no reports of aromatic six membered platinacycles. Complexes of the type (2.12) would therefore be of added interest in investigating the possibility of converting (2.12) into an unsaturated platinaanthracene (2.13).



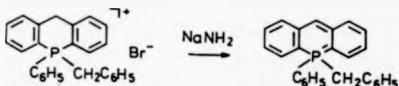
(2.12)



(2.13)

Protons have been abstracted from similar 9,10-dihydro heteroanthracenes to produce fully unsaturated anthracene type compounds<sup>265,266</sup> such as (2.15) in eq. 2.4.

eq. 2.4



(2.14)

(2.15)

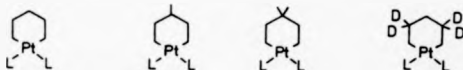
## 2.2 SYNTHESIS AND CHARACTERISATION OF SATURATED PLATINACYCLOHEXANES

The three platinacyclohexanes (2.16a), (2.17) and (2.18a) substituted at the 4-position, were synthesised initially to see how the presence of the square planar platinum atom and the

substituents would affect the conformation of the six membered ring. The conformation of the rings were studied by n.m.r. spectroscopy and X-ray crystallography.

The complexity of the  $^1\text{H}$  n.m.r. spectrum (Fig. 2.7) of platinacyclohexane (2.16a) due to the presence of  $^1\text{H}$ - $^1\text{H}$ ,  $^1\text{H}$ - $^{31}\text{P}$  and  $^1\text{H}$ - $^{195}\text{Pt}$  couplings, prompted the synthesis of the deuterated platinacyclohexane (2.19). It was reasoned that by isolating the  $\alpha$  and  $\gamma$  protons by chemical substitution of the  $\beta$  protons by deuterium, the  $^1\text{H}$  n.m.r. spectrum would be simplified by elimination of the couplings to the  $\beta$  protons.

Suitable crystals of the closely related unsubstituted platinacyclohexane (2.16b) were obtained to study the conformation of the ring by X-ray crystallography. To determine the effect of substitution on the ring the platinacyclohexane (2.18b) was synthesised and suitable crystals obtained so that a direct comparison could be made.



(2.16a)  $\text{L}=\text{PPh}_3$  (2.17)  $\text{L}=\text{PPh}_3$  (2.18a)  $\text{L}=\text{PPh}_3$  (2.19)  $\text{L}=\text{PPh}_3$

(2.16b)  $\text{L}=\text{PMe}_2\text{Ph}$

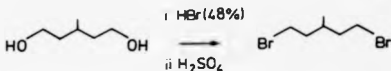
(2.18b)  $\text{L}=\text{PMe}_2\text{Ph}$

### 2.2.1 Synthesis of the 1,5-Dibromopentane Precursors

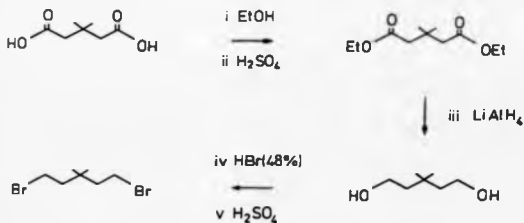
The 1,5-dilithiopentane and 1,5-bis(bromomagnesium)pentane reagents used in the synthesis of the platinacyclohexanes (2.16a), (2.16b), (2.17), (2.18a), (2.18b) and (2.19) (see Section 2.2.2) were prepared from the corresponding 1,5-dibromopentane.<sup>20</sup>

1,5-Dibromopentane was commercially available. 1,5-Dibromo-3-methylpentane was prepared from the diol by refluxing in a mixture of hydrobromic acid and sulphuric acid for three hours<sup>267</sup> (see eq. 2.5).

eq. 2.5



Several steps were involved in the synthesis of 1,5-dibromo-3,3-dimethylpentane.<sup>267,268,269</sup> 3,3-Dimethylglutaric acid was used as the starting material and the route used was that shown in Scheme 2.1.



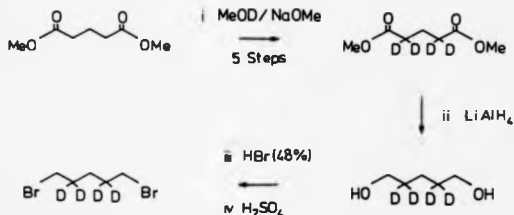
Scheme 2.1. Synthesis of 1,5-dibromo-3,3-dimethylpentane.

All the steps involved were modifications of literature methods<sup>267,268,269</sup> and the moderate yields obtained were not optimised. The yields of the 1,5-dilithiopentane reagents with alkyl substituents at the 3-position were lower than that of the unsubstituted 1,5-dilithiopentane. This may be due to the tendency of the substituted mono lithiated pentane to cyclise. The yield of the 1,5-dilithiopentane reagent also depended critically on the reaction conditions. Optimum yields were obtained using lithium with ca. 2% sodium content.

The yields of the dilithioalkane reagents were lower than the corresponding bis(bromomagnesium)alkane reagents. This may explain the higher yields of the platinacyclohexanes when the Grignard reagents were used. The activity of the alkylating agents appeared to be a critical factor in determining the yields of the resulting platinacyclohexanes.

The bis(bromomagnesium)alkane used in the synthesis of (2.19) (see Section 2.2.2) was made from the corresponding

1,5-dibromopentane-2,2,4,4- $d_4$  which was synthesised in three steps<sup>266,268,270</sup> as shown in Scheme 2.2. Diethylglutarate was used as starting material and was treated five times successively with methanol- $d_1$ . The deuterium incorporation of the  $\alpha$  protons was determined by  $^1H$  n.m.r. spectroscopy.

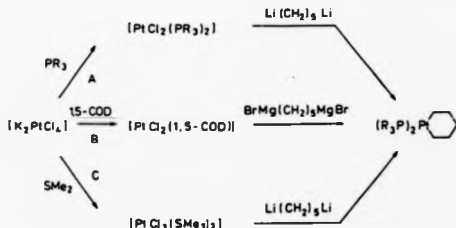


Scheme 2.2. Synthesis of 1,5-dibromopentane-2,2,4,4- $d_4$ .

The mass spectrum of 1,5-dibromopentane-2,2,4,4- $d_4$  was analysed to determine the extent of deuteration. The percentage deuterium content for the 1,5-dibromopentane was calculated to be 81.7%- $d_4$ , 15.0%- $d_3$ , 2.0%- $d_2$  and 0.6%- $d_1$  (equivalent to 95%- $d$  incorporation per site). These values were satisfactory for the spectral simplification of the resulting platinumcyclohexane (2.19).

### 2.2.2 Synthesis of the Platinacyclohexanes

Whitesides et al.<sup>20</sup> have reported the synthesis of saturated platinacyclohexanes by two general routes (see Scheme 2.3, routes A and B). In our hands treatment of  $[\text{PtCl}_2(\text{PR}_3)_2]$  with 1,5-dithiopentanes (Scheme 2.3, route A) gave poor yields and/or impure products (as shown by  $^{31}\text{P}\text{-}\{^1\text{H}\}\text{n.m.r.}$  spectroscopy). However, the platinacyclohexane  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2)_5]$  (2.16b) was prepared by this route and crystals suitable for X ray crystallography obtained. Treatment of  $[\text{PtCl}_2(1,5\text{-COD})]$  with 1,5-bis(bromomagnesium)pentanes followed by addition of  $\text{PR}_3$  (Scheme 2.3, route B) gave satisfactory yields of pure product. The platinacyclohexanes (2.16a), (2.17), (2.18a), (2.18b) and (2.19) were synthesized using this route. A modification of Whitesides' method,<sup>20</sup> using  $[\text{PtCl}_2(\text{SMe}_2)_2]$  as starting material was also used in the synthesis of the platinacyclohexanes (2.16a), (2.17) and (2.18a) (Scheme 2.3, route C).



Scheme 2.3. Synthesis of platinacyclohexanes using dithiopentanes and bis(bromomagnesium)pentane reagents.

The platinacyclohexanes (2.16a), (2.17), (2.18a) and (2.19) were all isolated as air stable, white, crystalline solids and were characterised by  $^1\text{H}$ ,  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $^{13}\text{C}$ - $\{^1\text{H}\}$  and  $^{195}\text{Pt}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy and by elemental analysis. Air stable yellow crystals were obtained for the more soluble dimethylphenylphosphine platinacyclohexanes (2.16b) and (2.18b). Chloroform solutions of the platinacyclohexanes decomposed over several hours to  $[\text{PtCl}_2(\text{PR}_3)_2]$ .

### 2.2.3 Spectroscopic Characterisation of Platinacyclohexanes

The  $^1\text{H}$  n.m.r. spectrum of (2.16a) (Fig. 2.7) (data given in Table 2.2) is complicated by the presence of the spin active  $^{31}\text{P}$  nuclei ( $I = \frac{1}{2}$ , 100%) and  $^{195}\text{Pt}$  ( $I = \frac{3}{2}$ , 33.4%). Two broad resonances centred at 1.20 and 1.42 ppm are assigned to the  $\alpha$  and  $\beta$  protons of the pentamethylene ring, respectively. A broad resonance is observed for the  $\gamma$  protons of the ring.

The  $^1\text{H}$  n.m.r. spectra of (2.17) and (2.18a) (data given in Table 2.2) are very similar to that of (2.16a) showing two broad resonances for the protons of the pentamethylene ring. However in the  $^1\text{H}$  n.m.r. spectrum of the 4-methyl derivative (2.17) the methyl resonance can be clearly seen as a doublet ( $J = 8 \text{ Hz}$ ) and in the spectrum of (2.18a), the 4,4-dimethyl derivative, the resonance for the two methyl groups is a singlet.

The complex multiplets for the methylene protons in compounds (2.16a), (2.17) and (2.18a) were not simplified by selective irradiation.

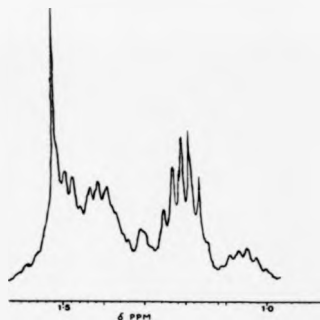


Fig. 2.7.  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ , 270 MHz) of  $[(\text{PPh}_3)_2\overline{\text{Pt}(\text{CH}_2)_5}]$ .

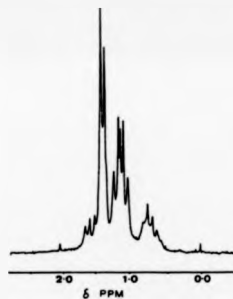


Fig. 2.8.  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ , 90 MHz) of  $(\text{PPh}_3)_2\overline{\text{Pt}(\text{CH}_2\text{CD}_2\text{CH}_2\text{CD}_2\text{CH}_2)}$ . (X = impurity).



The  $^1\text{H}$  n.m.r. spectrum of the tetradeuterated platinum-cyclohexane (2.19) is shown in Fig. 2.8 and the data given in Table 2.2. The resonance for the  $\alpha$  protons of the ring is a quartet with platinum satellites due to coupling to the two phosphorus nuclei and the spin active platinum. Coupling to the  $\gamma$  protons is not resolved. A broad singlet is observed for the  $\gamma$  proton resonance.

The  $^1\text{H}$  n.m.r. spectra of (2.16b) and (2.18b) (data given in Table 2.2) show two broad resonances for the pentamethylene protons, which are further complicated by the proton resonances of the dimethylphenylphosphine ligands.

$^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectroscopy has proved an invaluable method throughout this work for the determination of purity and structure of species in solution. The simplicity of the  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectra of the platinumacyclohexanes (2.16a) - (2.19) (data given in Table 2.3) is a great advantage. For example, the  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectrum of (2.16a) (see Fig. 2.9) is a singlet with  $^{195}\text{Pt}$  satellites. From this it can be deduced that the phosphorus nuclei are equivalent and, since  $^1\text{J}(\text{PtP})$  is small ( $\approx 2000$  Hz), trans to ligands of high trans-influence,<sup>271</sup> i.e. the pentamethylene moiety.

The  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectra of the platinumacyclohexanes (2.17), (2.18a) and (2.19) (data given in Table 2.3) are similar to that of (2.16a) showing only one species present in solution in which the two phosphorus nuclei are mutually cis, and trans to the pentamethylene moiety. The alkyl substituent at the 4-position of the platinumacyclohexane ring has little effect on the  $^{31}\text{P}$  chemical shift and the  $^1\text{J}(\text{PtP})$  coupling constant. This may be expected considering the distance from the substituents to the phosphorus nuclei.

Table 2.2.  $^1\text{H}$  n.m.r.<sup>a</sup> data for the platinumcyclohexanes (2.16a) - (2.19).

Compound	$\delta(\text{C}^1\text{H}_2\text{C}^2\text{H}_2\text{C}^3\text{H}_2)$	$\delta(\text{C}^4\text{H}_2)$	$\delta(\text{Ligand Resonances})$
(2.16a) <sup>b</sup>	1.20 (4H, m, $^2J(\text{PtH}) = 80.0 \text{ Hz}$ ), 1.42 (4H, m), 1.52 (2H, br s)	-	7.05-7.40 (m)
(2.16b)	broad multiplet in the range 1.10-1.72	-	1.46(m, $^2J(\text{PtH}) + ^4J(\text{PtH})$ , 8.8 Hz, $^3J(\text{PtH}) = 31.2 \text{ Hz}$ ), 7.18-7.66 (m)
(2.17) <sup>c</sup>	broad multiplet in the range 0.82-1.84	0.74 (d) $J=8 \text{ Hz}$	7.01-7.45 (m)
(2.18a) <sup>c</sup>	broad multiplet in the range 1.22-1.79	0.84 (s)	7.12-7.95 (m)
(2.18b)	broad multiplet in the range 0.94-1.76	0.82 (s)	1.45 (m, $^2J(\text{PtH}) + ^4J(\text{PtH})$ , 8.4 Hz, $^3J(\text{PtH}) = 31.8 \text{ Hz}$ ), 7.16-7.90 (m)
(2.19)	1.27 (4H, m, $^2J(\text{PtH}) = 79.0 \text{ Hz}$ ), $ J(\text{PtH}) + J(\text{Pt}, \text{H})  = 18.8 \text{ Hz}$ , 1.50 (2H, br s)	-	7.08-7.49 (m)

<sup>a</sup> Spectra (220 MHz) measured in  $\text{CDCl}_3$  at ambient temperature. Chemical shifts (t) ppm (t 0.01) to high frequency of  $\text{SiMe}_4$  and coupling constants (J) in Hz (t 0.1).

<sup>b</sup> Multiplicities: s = singlet, d = doublet, m = multiplet.

<sup>c</sup> Spectra measured at 400 MHz.

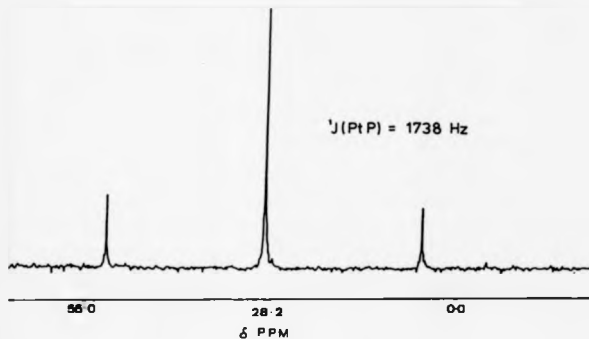


Fig. 2.9.  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum ( $\text{CDCl}_3$ , 36.4 MHz) of  
 $[(\text{PPh}_3)_2\text{Pt}(\overline{\text{CH}_2})_5]$ .

The  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectrum of (2.16a) is shown in Fig. 2.10 and the data given in Table 2.4. The resonance for the carbons shows coupling to both the platinum and the two phosphorus nuclei whereas the resonances for the  $\beta$  and  $\gamma$  carbons are singlets with  $^{195}\text{Pt}$  satellites. The resonance for the  $\delta$  carbons of the ring were definitively assigned by comparison with the  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectrum of the tetradeuterated platinacyclohexane (2.19) (data given in Table 2.4). The ring carbons carrying the deuterium atoms give rise to a low intensity multiplet due to coupling to  $^2\text{H}$  ( $I=1$ ).

Table 2.3.  $^{31}\text{P}$ - $^1\text{H}$  n.m.r.<sup>a</sup> and  $^{195}\text{Pt}$ - $^1\text{H}$  n.m.r.<sup>b</sup> data for  
platinacyclohexanes (2.16a) - (2.19).

Compound	$\delta(^{31}\text{P})$	$^1\text{J}(\text{PtP})$	$\delta(^{195}\text{Pt})$
(2.16a)	28.3	1738	-222
(2.16b)	-9.7	1676	-
(2.17)	28.3	1744	-243
(2.18a)	28.6	1732	-225
(2.18b)	-9.4	1672	-
(2.19)	28.2	1738	-

<sup>a</sup> Spectra (162 MHz) measured in  $\text{CDCl}_3$  at ambient temperature.

Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm 0.1$ ) to high frequency of

85%  $\text{H}_3\text{PO}_4$ . Coupling constant (J) are in Hz ( $\pm 3$ ).

<sup>b</sup> Spectra (85.6 MHz) measured in  $\text{CD}_2\text{Cl}_2$  at ambient temperature.

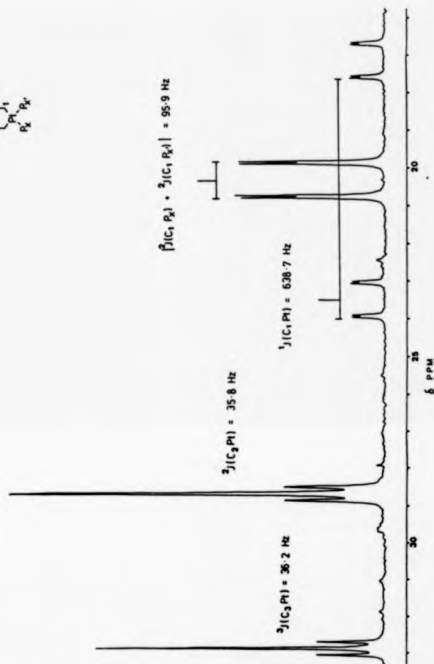


Fig. 2.10. Aliphatic region in the  $^{13}\text{C}$ - $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ , 100.6 MHz) of  $[(\text{PPh}_3)_3\text{Pt}(\text{CH}_2)_5]$ .

Table 2.4.  $^{13}\text{C}$ - $^1\text{H}$  n.m.r.<sup>a,b</sup> data for the platinumacyclic ring in compounds (2.16a)-(2.19).

Compound	$\delta(\text{C}^1)$	$ J(\text{C}^1\text{Pt}) - J(\text{C}^1\text{Pt}^*) $	$J(\text{C}^1\text{Pt})$	$\delta(\text{C}^2)$	$J(\text{C}^2\text{Pt})$	$\delta(\text{C}^3)$	$J(\text{C}^3\text{Pt})$	$\delta(\text{C}^4)$	$J(\text{C}^4\text{Pt})$
(2.16a)	20.3	95.9	638.7	26.7	35.8	32.9	36.2	-	-
(2.16b)	15.8	100.2	610.3	28.9	36.7	32.9	35.2	-	-
(2.17)	20.9	96.3	641.1	38.3	32.3	38.9	31.0	23.8	Not resolved
(2.18a)	16.4	90.7	642.6	33.5	26.8	41.7	Not resolved	29.8	Not resolved
(2.19)	20.1	95.5	640.0	27.9	Complex Multiplet	32.8	36.6	-	-

<sup>a</sup> Spectra (100.6 MHz) measured in  $\text{CDCl}_3$  at ambient temperature. Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm 0.1$ ) to high frequency of  $\text{SiMe}_4$  and coupling constants ( $J$ ) in Hz ( $\pm 0.1$ ).

<sup>b</sup> Data for  $^1\text{H}$  and resonances listed in Experimental Section E.2.1 in Table E.2.1.1.

Apart from this difference the spectra for (2.16a) and (2.19) were almost identical as would be expected.

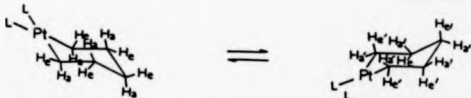
The  $^{13}\text{C}$ - $^1\text{H}$  n.m.r. spectra of the methyl substituted platinacyclohexanes (2.17) and (2.18a) (data given in Table 2.4) are similar to that of (2.16a), with the added presence of the resonance arising from the alkyl substituents on the ring.

## 2.3 CONFORMATIONAL STUDIES OF SATURATED PLATINACYCLOHEXANES

### 2.3.1 Solution N.M.R. Studies of $[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2)_5]$ , $[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{CD}_2\text{CH}_2\text{CD}_2\text{CH}_2)]$ and $[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$

Variable low temperature  $^1\text{H}$  n.m.r. spectra were measured for (2.16a) in a mixture of Freon-21 ( $\text{CHCl}_2\text{F}$ ) and Freon-22 ( $\text{CHClF}_2$ ). The spectra were obtained to investigate the possibility of ring reversal taking place on the n.m.r. timescale. It was hoped that a change in the spectrum would be observed as the axial and equatorial protons of the ring became inequivalent<sup>215</sup> on freezing out the two chair conformers in solution (eq. 2.6).

eq. 2.6



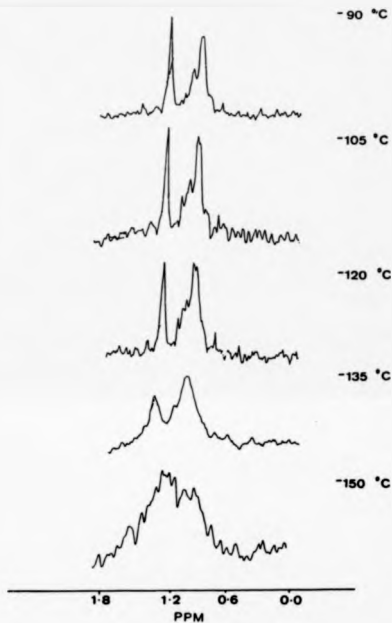


Fig. 2.11. Low temperature  $^1\text{H}$  n.m.r. spectra ( $\text{CHCl}_2\text{F} + \text{CHClF}_2$ , 400 MHz) of  $[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{CD}_2\text{CH}_2\text{CD}_2\text{CH}_2)]$ .



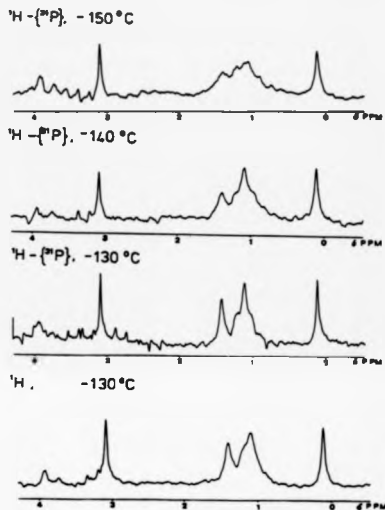


Fig. 2.12. Low temperature  $^1\text{H} - \{^{31}\text{P}\}$  n.m.r. spectra of  $(\text{CHCl}_2)^2 +$   
 $\text{CHClF}_2$ , 400 MHz of  $[(\text{Ph}_3\text{P})_2 \text{Pt}(\text{CH}_2\text{CD}_2\text{CH}_2\text{CD}_2\text{CH}_2)]$ .

However, the spectrum of (2.16a) at  $-160^{\circ}\text{C}$  and 400 MHz was very complex and little could be concluded because of the overlapping signals and complex  $^1\text{H}$ - $^1\text{H}$ ,  $^1\text{H}$ - $^{31}\text{P}$  and  $^1\text{H}$ - $^{195}\text{Pt}$  couplings. To avoid this problem the tetradeuterated platinacyclohexane (2.19) was made and its  $^1\text{H}$  n.m.r. and  $^1\text{H}$ - $^{31}\text{P}$  n.m.r. spectra measured at low temperature. On comparing Fig. 2.11 and Fig. 2.12 it can be seen that  $^{31}\text{P}$  decoupling did not result in significant simplification of the  $^1\text{H}$  n.m.r. spectra of (2.19). It is clear that at  $-150^{\circ}\text{C}$  and 400 MHz the signals are broadened (see Fig. 2.12). Unfortunately the slow exchange limit was not achieved because of the lack of solubility of the complex below  $-150^{\circ}\text{C}$ .

From previous studies the chemical shift difference  $\delta(\text{H}_{\text{axial}}) - \delta(\text{H}_{\text{equatorial}})$  would be expected to be 0.4 p.p.m. or 160 Hz (at 400 MHz). Hence an upper limit for  $\Delta G^{\ddagger}$  for ring reversal of (2.19) can be calculated to be  $20 \text{ kJ mol}^{-1}$ .<sup>272</sup> This is a lower energy barrier to ring reversal than any previously reported for a six membered ring and prompted the determination of the crystal structure of a platinacyclohexane. Suitable crystals of (2.16a) were not obtained but the closely related complex  $[(\text{PhMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2)_5]$  (2.16b) readily crystallized from dichloromethane/methanol (see Section 2.2.2).

It is known that the replacement of hydrogens by more bulky substituents on a six membered ring slows down ring reversal because the more severe 1,2 -diaxial interactions raise the activation energy.<sup>213</sup> Hence low temperature n.m.r. studies of 4,4-dimethyl platinacyclohexane (2.18a) were attempted. At the slow exchange limit, two resonances should be observed for the methyl

protons due to the presence of axial and equatorial methyl groups. However, as with the unsubstituted platinacyclohexane (2.16a), the slow exchange limit was not attained although broadening of the methyl resonance was observed.

From previous studies the chemical shift difference  $\delta(C_{\text{axial}}) - \delta(C_{\text{equatorial}})$  would be expected to be greater than the chemical shift difference  $\delta(H_{\text{axial}}) - \delta(H_{\text{equatorial}})$ . Hence the variable low temperature  $^{13}\text{C}$ - $^1\text{H}$  n.m.r. spectra were recorded of (2.18a). It was hoped that at low temperatures two methyl resonances would be apparent for the axial and equatorial methyl groups. Significant broadening was observed at  $-130^\circ\text{C}$  and 100.6 MHz but the slow exchange limit was not reached.

The crystal structure of  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$  (2.18b) was determined so that direct comparison with (2.16b) could be made.

### 2.3.2 X-Ray Crystal Structure of $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2)_5]$ and $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$

Selected bond lengths and angles with numbering scheme based on (2.16b) are listed in Table 2.5 and Table 2.6, and information on deviations from planes in Table 2.7. For platinacyclohexane (2.16b), only the major positions (see Experimental E.2.2) of the ring carbons are considered.

In the platinacyclohexane (2.16b) the square planar geometry around the platinum atom is slightly distorted (see Fig. 2.14). This is seen in the displacement of the ring carbon atoms from the plane defined by [Pt, P(1), P(2)] where C(1) is 0.34 Å to one

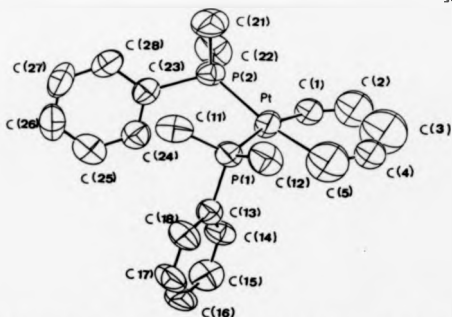


Fig. 2.13. The molecule of  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2)_5]$  showing the atomic numbering scheme (50% probability ellipsoids).

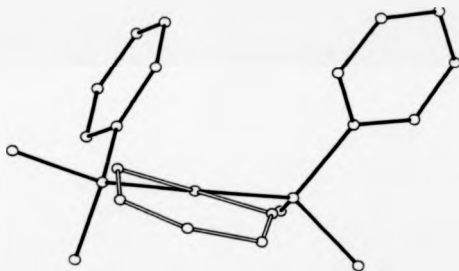


Fig. 2.14. An end on view of the platinacyclohexane ring in  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2)_5]$ .

Table 2.5. Bond distances (Å) and bond angles (°) for the platinumoclohexane (2.16b)

[(PMe <sub>2</sub> Ph) <sub>2</sub> Pt(Ch <sub>2</sub> S)] <sup>+</sup>			
Bond distances (Å)			
Pt-P(1)	2.269 (3)	Pt-P(2)	2.268 (4)
Pt-C(1)	2.195 (16)	Pt-C(5)	2.097 (34)
P(1)-C(11)	1.798 (10)	P(1)-C(12)	1.826 (19)
P(1)-C(13)	1.832 (10)	P(2)-C(21)	1.809 (11)
P(2)-C(22)	1.826 (18)	P(2)-C(23)	1.827 (10)
C(1)-C(2)	1.258 (28)	C(2)-C(3)	1.443 (44)
C(1)-C(4)	1.258 (23)	C(4)-C(5)	1.226 (31)
C(13)-C(14)	1.316 (33)	C(3)-C(16)	1.374 (15)
C(13)-C(15)	1.309 (43)	C(13)-C(18)	1.350 (19)
C(14)-C(15)	1.375 (16)	C(17)-C(18)	1.360 (14)
C(16)-C(17)	1.364 (20)	C(23)-C(28)	1.366 (15)
C(23)-C(24)	1.391 (14)	C(25)-C(26)	1.340 (16)
C(24)-C(25)	1.365 (16)	C(27)-C(28)	1.364 (18)
C(26)-C(27)	1.342 (17)		

Table 2.5. (continued)

Bond angles (°)	
P(1)-Pc-P(2)	98.1 (5)
P(2)-Pc-C(1)	91.3 (5)
P(2)-Pc-C(5)	170.5 (4)
Pc-P(1)-C(12)	104.5 (5)
Pc-P(1)-C(13)	102.5 (5)
Pc-P(2)-C(21)	109.5 (6)
Pc-P(2)-C(22)	106.2 (6)
C(12)-P(1)-C(13)	123.2 (3)
C(21)-P(2)-C(22)	123.2 (3)
C(12)-P(1)-C(13)	118.9 (10)
P(1)-Pc-C(1)	167.0 (4)
P(1)-Pc-C(5)	96.6 (9)
Pc-P(1)-C(11)	95.5 (11)
Pc-P(1)-C(13)	122.4 (5)
Pc-P(1)-C(13)	113.7 (4)
C(12)-P(1)-C(13)	102.1 (6)
Pc-P(2)-C(22)	116.1 (5)
Pc-P(2)-C(21)	121.6 (5)
Pc-P(1)-C(12)	121.6 (5)
Pc-P(1)-C(13)	122.4 (5)
C(12)-P(1)-C(13)	118.9 (10)
C(12)-P(1)-C(13)	122.0 (11)
C(26)-C(25)-C(28)	122.0 (11)
C(26)-C(27)-C(28)	122.0 (11)
C(13)-C(14)-C(15)	118.7 (3)
P(1)-C(13)-C(14)	119.3 (6)
P(1)-C(13)-C(15)	118.7 (3)
C(13)-C(14)-C(15)	118.7 (3)
C(13)-C(14)-C(17)	150.9 (11)
C(13)-C(18)-C(17)	120.1 (11)
P(2)-C(21)-C(28)	123.7 (6)
C(23)-C(24)-C(25)	120.7 (10)
C(25)-C(26)-C(27)	119.6 (12)
C(23)-C(24)-C(28)	118.9 (10)
C(26)-C(25)-C(28)	122.0 (11)
C(26)-C(27)-C(28)	122.0 (11)

side and C(5) 0.30 Å to the other. However, C(1), C(2), C(4) and C(5) are themselves coplanar. The conformation of the ring is a half chair (Fig. 2.15) with the platinum atom below this plane (0.75 Å) and C(3) slightly above it (0.15 Å). The flattening of the platinacyclic ring in (2.16b) may be expected to lead to a lower energy barrier to ring reversal. This is observed in low temperature n.m.r. studies of (2.16a) which may indicate that the structures of the two platinacycles (2.16a) and (2.16b) are similar in the solid state and in solution.

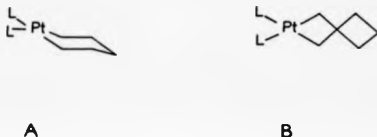


Fig. 2.15. Half chair (A) and skew (B) conformations of platinacyclohexane rings.

In the 4,4-dimethylplatinacyclohexane (2.16b) the square planar geometry around the platinum atom is also slightly distorted (Fig. 2.17). This can again be seen from the displacement of the ring carbons from the plane defined by Pt, P(1), P(2) where C(1) is 0.17 Å to one side and C(5) is 0.04 Å to the other.

The conformation of the platinacyclohexane ring is skew (Fig. 2.17) where the ring is twisted about C(2) and C(4). The twisting is not symmetrical, C(4) is displaced 0.81 Å above the plane defined by [Pt, C(1), C(5)] and C(2) 0.55 Å below it.

The effect of twisting of the ring about C(2) and C(4) probably alleviates the non bonded interactions between the hydrogens on C(2) and C(4) and the methyl groups on C(3).

Unlike the partial disorder found in (2.16b), the substituted platinacyclohexane (2.16b) is ordered in the crystal. However, the methyl groups have large thermal parameters in directions tangential to the ring (see Fig. 2.18). These are probably dynamic in origin, rather than arising from disorder, because the thermal parameters of the ring atoms show no unusual features.

Unfortunately, low temperature n.m.r. studies did not freeze out the two conformers of either of the two platinacyclic rings in (2.16a) or (2.16b) and so it cannot be determined whether the greater rigidity of (2.16b) in the crystal is reflected in solution.

The presence of the methyl groups causes a change in the conformation of the platinacyclohexane ring from a half chair in (2.16b) to skew in (2.16b) (Fig. 2.15). A significant feature is the higher degree of puckering in the platinacyclohexane ring in (2.16b) in comparison to (2.16b). This puckering is detected in the torsion angles Pt-C(1)-C(2)-C(3), C(2)-C(3)-C(4)-C(5) and C(3)-C(4)-C(5)-Pt of (2.16b) compared to those in (2.16b) (data given in Table 2.8). However, both are flattened in comparison to cyclohexane itself where the torsional angles in the ring are 50°. 199



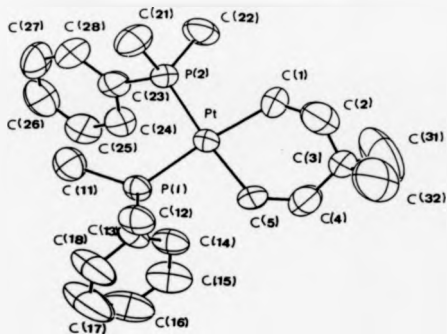


Fig. 2.16. The molecule of  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$  showing the atomic numbering scheme (50% probability ellipsoids).

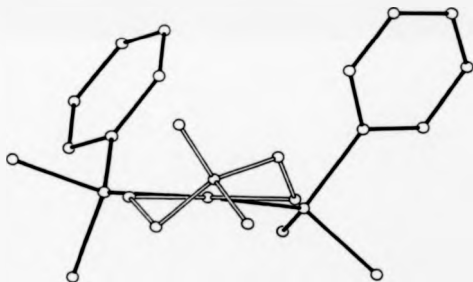


Fig. 2.17. An end on view of the platinacyclohexane ring in  $[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$ .

**Table 2.6.** Bond distances (Å) and bond angles (°) for the platinumocyclohexane (2.186)  
 $[(Ph_2Pt)_2Fe(CH_2CH_2C(CH_3)_2CH_2CH_2)]$ .

Bond distances (Å)			
Pt(1)-P(1)	2.290 (3)	Pt(1)-P(2)	2.273 (3)
Pt(1)-C(5)	2.089 (13)	Pt(1)-C(11)	2.102 (13)
P(1)-C(13)	1.833 (10)	P(1)-C(11)	1.852 (18)
P(1)-C(12)	1.809 (13)	P(2)-C(22)	1.818 (16)
P(2)-C(21)	1.824 (12)	P(2)-C(23)	1.834 (11)
C(23)-C(24)	1.363 (17)	C(23)-C(28)	1.391 (14)
C(24)-C(25)	1.396 (21)	C(25)-C(26)	1.368 (19)
C(26)-C(27)	1.380 (22)	C(27)-C(28)	1.384 (17)
C(13)-C(14)	1.360 (18)	C(13)-C(18)	1.371 (17)
C(14)-C(15)	1.385 (23)	C(15)-C(16)	1.308 (26)
C(16)-C(17)	1.388 (26)	C(17)-C(18)	1.368 (17)
C(4)-C(13)	1.483 (18)	C(5)-C(4)	1.498 (18)
C(2)-C(11)	1.548 (26)	C(2)-C(3)	1.503 (21)
C(3)-C(2)	1.503 (21)	C(3)-C(4)	1.483 (18)
C(3)-C(32)	1.505 (39)	C(3)-C(31)	1.420 (33)
C(32)-C(3)	1.505 (39)	C(1)-C(2)	1.548 (26)

Table 2.6. (continued)

Bond Angles (°)	
P(1)-Pt(1)-P(2)	97.9 (1)
P(2)-Pt(1)-C(5)	174.6 (4)
P(2)-Pt(1)-C(1)	88.5 (4)
P(1)-Pt(1)-C(1)	114.4 (4)
C(1)-Pt(1)-C(1)	101.9 (6)
C(1)-Pt(1)-C(1)	102.1 (5)
P(1)-Pt(1)-C(2)	118.3 (4)
C(2)-Pt(1)-C(2)	99.7 (7)
C(2)-Pt(1)-C(3)	96.4 (7)
P(2)-Pt(1)-C(3)	132.5 (8)
C(2)-Pt(1)-C(3)	119.4 (11)
C(2)-Pt(1)-C(2)	120.6 (14)
C(2)-Pt(1)-C(2)	118.9 (11)
P(1)-C(1)-C(1)	121.8 (10)
C(1)-C(1)-C(1)	118.3 (11)
C(1)-C(1)-C(1)	117.2 (16)
C(1)-C(1)-C(1)	117.7 (13)
P(1)-C(1)-C(1)	114.6 (12)
C(1)-C(1)-C(1)	109.7 (14)
C(1)-C(1)-C(1)	115.9 (15)
C(1)-C(1)-C(1)	109.2 (16)
C(1)-C(1)-C(1)	100.1 (19)
P(1)-Pt(1)-C(5)	87.4 (4)
P(1)-Pt(1)-C(1)	172.0 (5)
C(5)-Pt(1)-C(1)	86.5 (4)
P(1)-Pt(1)-C(1)	114.2 (4)
C(1)-Pt(1)-C(1)	121.2 (7)
C(1)-Pt(1)-C(1)	120.6 (12)
P(1)-Pt(1)-C(2)	114.6 (4)
C(2)-Pt(1)-C(2)	116.8 (4)
C(2)-Pt(1)-C(3)	116.8 (5)
P(2)-Pt(1)-C(3)	117.5 (9)
C(2)-Pt(1)-C(3)	119.7 (11)
C(2)-Pt(1)-C(2)	120.3 (13)
C(2)-Pt(1)-C(2)	121.1 (12)
C(1)-C(1)-C(1)	119.6 (15)
C(1)-C(1)-C(1)	122.1 (15)
C(1)-C(1)-C(1)	123.7 (15)
C(1)-C(1)-C(1)	120.6 (13)
C(1)-C(1)-C(1)	119.6 (11)
C(1)-C(1)-C(1)	115.3 (11)
C(1)-C(1)-C(1)	111.4 (19)
C(1)-C(1)-C(1)	102.6 (16)
P(1)-C(1)-C(1)	119.2 (13)

**Table 2.7.** Deviations ( $\text{\AA}$ ) from mean planes (defined by starred atoms; e.s.d.'s  $\pm 0.05 \text{\AA}$ ).

Compound (2.16b)							
*Pt	0.00	*P(1)	0.00	*P(2)	0.00	C(1)	-0.34
C(2)	0.26	C(3)	0.71	C(4)	0.87	C(5)	0.30
Pt	0.75	*C(1)	0.00	*C(2)	0.00	C(3)	0.15
*C(4)	0.00	*C(5)	0.00				
Compound (2.18b)							
*Pt	0.00	*P(1)	0.00	*P(2)	0.00	C(1)	0.17
C(2)	-0.76	C(3)	-0.20	C(4)	0.76	C(5)	0.04
*Pt	0.00	*C(1)	0.00	C(2)	-0.55	C(3)	0.37
C(4)	-0.81	*C(5)	0.00				

**Table 2.8.** Comparison of dihedral angles ( $^\circ$ ) of Type 1 for platina-cyclohexane ring.

Compound	(2.16b)			(2.18b)
Pt C(1)	C(2)	C(3)	29.3	69.1
C(1) C(2)	C(3)	C(4)	-15.6	-47.3
C(2) C(3)	C(4)	C(5)	16.5	-20.5
C(3) C(4)	C(5)	Pt	-35.6	66.8
C(4) C(5)	Pt	C(1)	38.7	-36.4
C(5) Pt	C(1)	C(2)	-32.8	-24.1

## 2.4 DISCUSSION

The conformational studies of the platinacyclohexanes show that replacement of a single methylene unit (requiring a bond angle of ca  $109^\circ$  in its tetrahedral geometry) in cyclohexane, by the larger platinum atom (requiring a greatly reduced angle of  $90^\circ$  in its square planar geometry) and its ligated atoms, results in flattening of the six membered ring with respect to cyclohexane.

The crystal structures of some saturated platinacyclopentanes and platinacyclobutanes have shown that the presence and number of substituents and the bulkiness and crowding of the other ligands do influence the conformation of the ring.<sup>93</sup> Puckering of the ring is effective in reducing the intraring strain. Thus the replacement of two hydrogens in platinacyclohexane (2.16b) by two methyl groups at the 4-position on the platinacyclohexane ring in (2.18b) changes the conformation of the ring from a half chair in (2.16b) to the more puckered skew in (2.18b). However the conformation of (2.18b) is still flattened in comparison to cyclohexane.

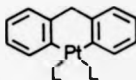
The crystal structures of the two platinacyclohexanes (2.16b) and (2.18b) and the results obtained in the variable temperature n.m.r. studies are consistent with a lowering of the energy barrier to ring reversal. From the results of the n.m.r. studies, an upper limit for  $\Delta G^\ddagger$  for ring reversal of the unsubstituted platinacyclohexane was calculated to be  $\sim 20 \text{ kJ mol}^{-1}$ .<sup>272</sup> This is a lower energy barrier to ring reversal than any previously reported for a six membered heterocyclic ring.

The torsional arrangements of the ring atoms in cyclohexane are altered by replacement of a methylene unit by a platinum atom.

The low energy barrier may be due to a lower barrier to torsion of the C-Pt bond as compared to the C-C bond. However no values are known for the former and therefore such a correlation can only be tentative.

## 2.5 SYNTHESIS AND CHARACTERISATION OF UNSATURATED 9,10-DIHYDRO-9-PLATINAANTHRACENES

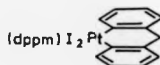
The platinum(II) complexes (2.20a - h) and the related platinum (IV) complexes (2.21) and (2.22) are of interest for two reasons: (i) to determine the effect the square planar platinum(II) atom and the octahedral platinum(IV) atom, and their ligands have on the conformation of the central ring; (ii) to investigate the possibility of aromatisation of the platinacyclic ring.



(2.20a)	$L = \text{PEt}_3$	(2.20e)	$L = \text{PPh}_3$
(2.20b)	$L = \text{PMe}_3$	(2.20f)	$L_2 = 1,5\text{-COD}$
(2.20c)	$L = \text{PMe}_2\text{Ph}$	(2.20g)	$L_2 = \text{dppm}$
(2.20d)	$L = \text{PMePh}_2$	(2.20h)	$L_2 = \text{dppa}$



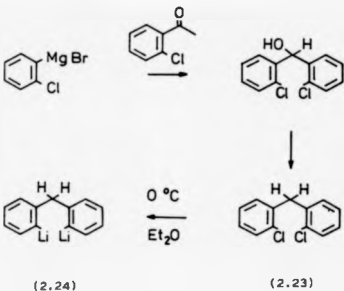
(2.21)



(2.22)

#### 2.5.1 Synthesis of 2,2'-Dichlorodiphenylmethane

In several of the methods<sup>239</sup> used to synthesise 9,10-dihydroheteroanthracenes the diGrignard reagent of 2,2'-dichlorodiphenylmethane is used. However the preparation of this diGrignard is difficult to initiate and involves refluxing the mixture for several days. In the present work 2,2'-dilithiodiphenylmethane (2.24) is used in the synthesis of the 9,10-dihydro-9-platinoanthracenes. The synthetic route to 2,2'-dibromodiphenylmethane is relatively long and low yielding<sup>238,273</sup> and so 2,2'-dichlorodiphenylmethane (2.23) was synthesised and used in the preparation of 2,2'-dilithiodiphenylmethane as shown in Scheme 2.4.<sup>273,274</sup>

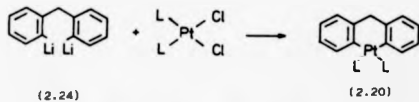


**Scheme 2.4.** Synthesis of 2,2'-dilithiodiphenylmethane.

### 2.5.2 Synthesis of the 9,10-Dihydro-9-platinoanthracenes

The 9,10-dihydro-9-platinaanthracenes (2.20a-f) were synthesised by treatment of the appropriate  $[PtCl_2L_2]$  complex with 2,2'-dilithiodiphenylmethane (2.24) (eq. 2.7).

eq. 2.7



L = PEt<sub>3</sub>, PMe<sub>3</sub>, PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, PPh<sub>3</sub>, 1,5-COD



The activity of 2,2'-dilithiodiphenylmethane was determined by a modification of Gilman's double titration method<sup>275</sup> and appeared to affect the yield of the platinacycle. The surface area, sodium content of the lithium, temperature of the mixture and reaction time were all critical in determining the activity. The preparation of the 2,2'-dilithiodiphenylmethane was repeated several times to optimise the conditions and activity.

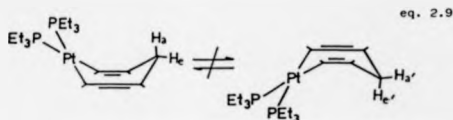
The 9,10-dihydro-9-platinaanthracenes were isolated as air stable solids which were characterised by  $^1\text{H}$ ,  $^{31}\text{P}$ - $\{^1\text{H}\}$ ,  $^{13}\text{C}$ - $\{^1\text{H}\}$  and  $^{195}\text{Pt}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy and elemental analysis. The platinacycle  $[(1,5\text{-COD})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20f) was isolated at  $-78^\circ\text{C}$  as a bright yellow solid which was stable at room temperature and was characterised by  $^1\text{H}$  and  $^{13}\text{C}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy. Both platinacycles  $[(\text{dppm})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20g) and  $[(\text{dppe})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20h) were synthesised from compound (2.20f) by substitution of 1,5-cyclooctadiene with the required phosphine (eq. 2.8). This method was used to make the 9,10-dihydro-9-platinaanthracenes with a range of phosphine ligands.

eq. 2.8



### 2.5.3 Spectroscopic Characterisation of 9,10-Dihydro-9-Platinaanthracenes

The  $^1\text{H}$  n.m.r. data for the 9,10-dihydro-9-platinaanthracenes (2.20a-h) are given in Table 2.9. Two features of the  $^1\text{H}$  n.m.r. spectrum of platinacycle (2.20a) (Fig. 2.18) are interesting. Firstly it was surprising to see two resonances for the methylene protons of the platinacyclic ring centred at 63.34 and 64.25 ppm. Assuming the ring adopted a boat conformation, the observation that these two methylene protons were chemically inequivalent indicated that conformers of the ring were not interconverting rapidly in solution (eq. 2.9) on the n.m.r. timescale at ambient temperature.



This would suggest that substitution of a platinum atom in the ring has significantly increased the energy barrier to ring reversal.

The resonances attributed to the methylene protons of the ring were complicated by the presence of  $^{195}\text{Pt}$  satellites. The two proton resonances exhibit different long range four bond  $J(\text{Pt}-\text{H})$  coupling constants as a result of a geometrical type dihedral angle effect<sup>276</sup> (Fig. 2.19).



Fig. 2.18. ( $^1\text{H}$ ) n.m.r. spectrum ( $\text{CDCl}_3$ , 400 MHz) of  $[(\text{PEt}_3)_2\text{Si}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (X = impurity).

Table 2.9.  $^1\text{H}$  n.m.r. data for compounds (2), (3a-b) and (2', 3').

[illegible]

Table 2.9. (continued)

[illegible]

<sup>a</sup> Spectra (220 MHz) measured in benzene-*d*<sub>6</sub> at ambient temperature. Chemical shifts (δ) in p.p.m. (± 0.01) to high frequency of TMS. <sup>b</sup>  $J_{\text{H-F}}$  and coupling constants (*J*) are in Hz (± 0.1). Multiplicities: s = singlet, t = virtual triplet, m = multiplet. <sup>c</sup> Not fully resolved.

<sup>c</sup> Spectra (400 MHz) measured in benzene-*d*<sub>6</sub>.



$$^4J(\text{PtH}_1) = 16.4 \text{ Hz}$$

$$^4J(\text{PtH}_2) = 5.5 \text{ Hz}$$

$$^2J(\text{H}_1\text{H}_2) = 12.4 \text{ Hz}$$

Fig. 2.19. The rigid boat conformation renders the two methylene protons  $\text{H}_1$  and  $\text{H}_2$  chemically inequivalent.

The second interesting feature of the  $^1\text{H}$  n.m.r. spectrum of (2.20a) was the presence of two resonances for the methylene protons of the triethylphosphine ligands. Two explanations were considered which could account for this. The first was that the methylene groups on each phosphine ligand were chemically inequivalent. This could only arise if the two phosphorus nuclei were chemically inequivalent, but the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of (2.20a) (data given in Table 2.10) showed only a single resonance.

A second explanation was that the two protons of the  $\text{PCH}_2$  group were chemically inequivalent. A two-dimensional correlation spectrum (COSY) was recorded to determine if this was indeed the case. The presence of off diagonal cross peaks (Fig. 2.20) showed that the two protons were chemically inequivalent and were coupled to each other. The two methylene protons are in fact diastereotopic<sup>277</sup> because the boat conformation is rigid in solution on the n.m.r. timescale.

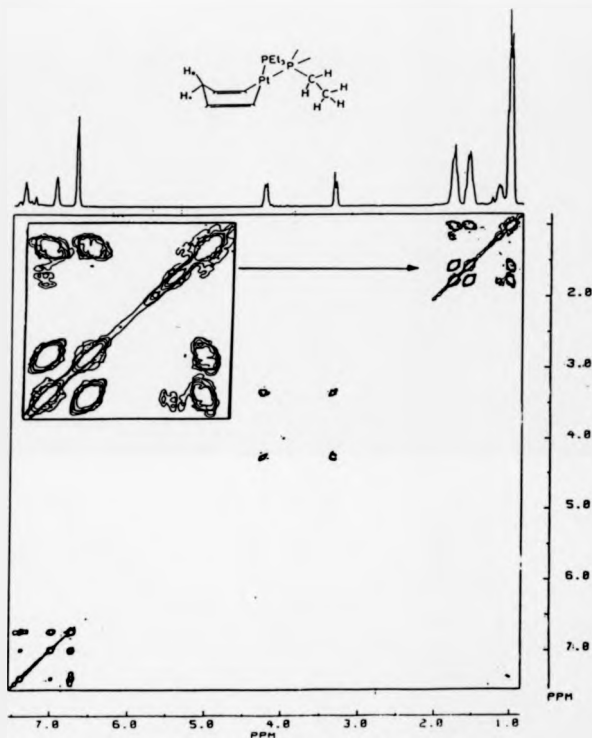


Fig. 2.20. Two Dimensional Correlation Spectrum ( $\text{CDCl}_3$ , 400 MHz)



The  $^1\text{H}$  n.m.r. spectra of the 9,10-dihydro-9-platinaanthracene compounds (2.20b-a) are similar to that of (2.20a) in that they show the platinacyclic ring is rigid and the conformers are not interconverting in solution on the n.m.r. timescale. Two resonances were observed for the diastereotopic methyl groups in the dimethylphenylphosphine complex (2.20c).

The  $^1\text{H}$  n.m.r. spectrum of (2.20b) (Fig. 2.21) shows separate resonances for each of the aromatic ring protons of the 9,10-dihydro- 9-platinaanthracene and the triphenylphosphine ligands. Selective decoupling experiments enabled assignment of the individual protons and information on all the couplings to be obtained (data given in Table 2.9).

The high energy barrier to ring reversal in compounds (2.20a-e) must be due to the presence of the platinum atom. The square planar geometry of the platinum centre constrains the ligated phosphorus and carbon atoms to the same plane and it is thus inevitable that the substituents on the phosphine will be subject to non bonded interactions with the peri protons on the aromatic rings of the 9,10-dihydroanthracene moiety. It is this interaction (Fig. 2.22) which is most likely the reason for the high activation energy of ring reversal. Less bulky ligands would be expected to lead to a lower energy barrier. In compounds (2.20f) and (2.20g) the 1,5-cyclooctadiene ligand and the bis(diphenylphosphino)methane (dppm) are chelating and are less sterically demanding than the unidentate phosphines.



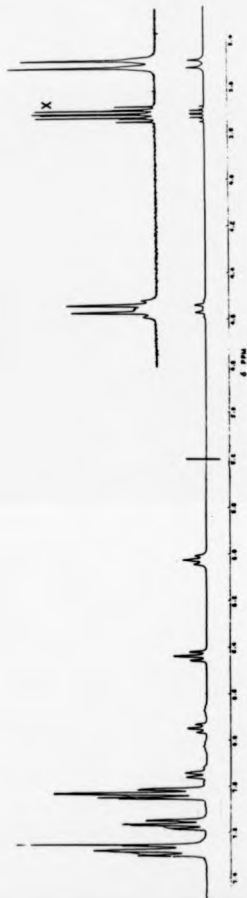


Fig. 2.21.  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ , 400 MHz) of  $[(\text{PPh}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$   
(X = impurity).

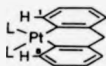


Fig. 2.22. Proposed planar transition state of ring reversal of compounds (2.20a-e) in which ligands L will be subjected to non bonded interactions with the peri protons on C(1) and C(8).

The  $^1\text{H}$  n.m.r. spectrum of  $[(1,5\text{-COD})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20f) and  $[(\text{dppm})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20g) showed only one resonance for the methylene protons of the platinacyclic ring. This indicated that the ring was either undergoing rapid ring reversal on the n.m.r. timescale or the compound was a static planar one. In view of the number of conformational studies of 9,10-dihydro-9-heteroanthracenes that show rapid ring reversal of the boat conformation,<sup>260,263</sup> the latter case was considered unlikely. The  $^1\text{H}$  n.m.r. of  $[(\text{dppe})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20h) shows two resonances for the methylene protons, indicating that the boat conformations are rigid in solution. Thus increasing the carbon backbone of the bis(diphenylphosphino)methane ligand in (2.20f) by one carbon to the more sterically demanding 1,2-bis(diphenylphosphino)ethane

Table 2.10.  $^{31}\text{P}\text{--}({}^1\text{H})$  <sup>a</sup> and  $^{195}\text{Pt}\text{--}({}^1\text{H})$  <sup>b</sup> n.m.r. data for the compounds (2.20a-h), (2.21) and (2.22).

Compound	$\delta$ ( $^{31}\text{P}$ )	$^1\text{J}(\text{PtP})$	$\delta$ ( $^{195}\text{Pt}$ )
(2.20a)	4.3	1833	-52.2
(2.20b)	-26.1	1779	6.6
(2.20c)	-13.1	1845	-30.0
(2.20d)	3.8	1856	-28.9
(2.20e)	22.9	1890	-29.7
(2.20g)	-33.1	1466	-
(2.20h)	44.6	1818	-
(2.21)	-20.0	1782	847.2
(2.22)	-31.0	954	-

<sup>a</sup> Spectra (162 MHz) measured in  $\text{CDCl}_3$  at ambient temperature.

Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm 0.1$ ) to high frequency of 85%  $\text{H}_3\text{PO}_4$ . Coupling constants ( $\text{J}$ ) in Hz ( $\pm 3$ ).

<sup>b</sup> Spectra (85.6 MHz) measured in  $\text{CDCl}_3$  at ambient temperature.

Chemical shift ( $\delta$ ) in p.p.m.

(dppe) has increased the energy barrier to ring reversal. This is a result of the unfavourable steric interactions between the peri protons and the ligand which are encountered in the transition state.

The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. and  $^{195}\text{Pt}\{-^1\text{H}\}$  n.m.r. data for compounds (2.20a-h) are listed in Table 2.10. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra of the 9,10-dihydro-9-platinaanthracene compounds are all similar in that they show a singlet resonance with  $^{195}\text{Pt}$  satellites. The  $^1\text{J}(\text{PtP})$  values indicate that the two phosphines are mutually cis, and trans to a ligand which exerts a high trans-influence. The  $^{31}\text{P}$  and  $^{195}\text{Pt}$  chemical shifts and  $^1\text{J}(\text{PtP})$  values are all affected by the nature of the phosphine ligands present.

The  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectra for compounds (2.20) (data given in Table 2.11) are all similar; the spectrum of the triethylphosphine platinum(II) complex (2.20) shows that the two ligating carbon atoms of the 9,10-dihydroanthracene moiety C(12) and C(13) are coupled to both the spin active platinum atom and the two phosphorus nuclei. Coupling to the platinum atom is observed in the resonances attributed to six of the carbon atoms of the aromatic rings of the 9,10-dihydroanthracene moiety. The other four carbon resonances are singlets. The methylene carbon atom C(10) is also coupled to the platinum atom (see Fig. 2.23).

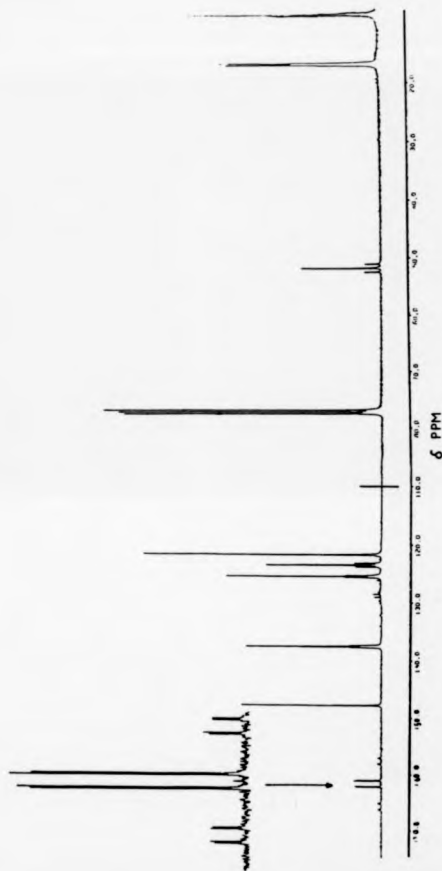
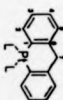


Fig. 2.2 3.  $^{13}\text{C}$ - $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ , 100.6 MHz) of  $[(\text{PEt}_3)_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4]$ .

Table 2.11.  $^{13}\text{C}-\{^1\text{H}\}$  n.m.r. <sup>a,b</sup> data for compounds (2,20a-f) and 2,21.

Compound	$\delta(\text{C}^1)$	$^1_J(\text{C}^1\text{Pr})$	$^2_J(\text{C}^1\text{P})$	$\delta(\text{C}^2-\text{C}^6)$	$\delta(\text{C}^7)$	$^3_J(\text{C}^7\text{Pr})$
(2,20a)	161.5	806.5	116.7	121.5 (s),	51.6	138.4
				123.3 (t, $J(\text{CP})=60.9$ Hz),		
				125.3 (t, $J(\text{CP})=34.8$ Hz),		
				137.3 (t, $J(\text{CP})=7.4$ Hz),		
				147.5 (s),		
(2,20b)	159.9	799.9	120.7	122.1 (s),	51.8	136.6
				123.3 (t, $J(\text{CP})=60.3$ Hz),		
				125.4 (t, $J(\text{CP})=34.3$ Hz),		
				138.1 (t, $J(\text{CP})=8.90$ Hz),		
				146.8 (s),		
(2,20c)	159.7	813.7	119.4	122.2 (s),	52.0	135.0
				123.5 (t, $J(\text{CP})=60.5$ Hz),		
				125.5 (t, $J(\text{CP})=34.2$ Hz),		
				138.3 (br s), 146.29 (s),		
				146.8 (s),		
(2,20d)	159.7	812.9	119.9	122.2 (s),	51.9	137.5
				123.5 (t, $J(\text{CP})=59.9$ Hz),		
				123.4 (t, $J(\text{CP})=34.6$ Hz),		
				138.3 (t, $J(\text{CP})=9.6$ Hz),		
				146.3 (s),		

Table 2.11. (continued)

Compound	$\delta(\text{C}^1)$	$^1J(\text{C}^1\text{Pt})$	$^2J(\text{C}^1\text{P})$	$\delta(\text{C}^2-\text{C}^6)$	$\delta(\text{C}^7)$	$^3J(\text{C}^7\text{Pt})$
(2.20e)	159.0	850.3	114.4	121.4 (s), 123.7 (t, $J(\text{CPT})=66.2$ Hz), 124.6 (t, $J(\text{CPT})=57.3$ Hz), 129.2 (t, $J(\text{CPT})=59.9$ Hz), 145.4 (br m).	52.1	139.1
(2.20f)	153.6	Not Resolved	-	124.2 (s), 125.7 (t, $J(\text{CPT})=65.5$ Hz), 126.5 (t, $J(\text{CPT})=49.2$ Hz), 134.6 (s), 142.3 (s).	51.1	144.8
(2.21)	146.1	Not Resolved	-	125.9 (t, $J(\text{CPT})=45.9$ Hz), 126.4 (s), 128.2 (t, $J(\text{CPT})=33.6$ Hz), 137.0 (s), 143.7 (s).	50.3	61.1

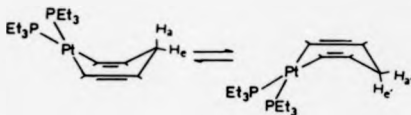
<sup>a</sup> Spectra (100.6 MHz) measured in  $\text{CDCl}_3$  at ambient temperature. Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm 0.1$ ) relative to  $\text{SiMe}_4$ . Coupling constants ( $J$ ) in Hz ( $\pm 0.1$ ). Multiplicities: s = singlet; t = virtual triplet; m = multiplet.

<sup>b</sup> Data for  $^1\text{J}$  and resonances listed in Experimental Section E.2.1 in Table E.2.1.3.

2.6 CONFORMATIONAL STUDIES OF  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$ 2.6.1 Solution N.M.R. Studies of  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$ 

Variable high temperature  $^1\text{H}$  n.m.r. spectra were measured for (2.20a) in  $\text{DMSO}-d_6$ . The spectra were recorded to investigate the possibility of the boat conformation of the platinacyclic ring undergoing ring reversal on the n.m.r. timescale (eq. 2.10). Coalescence of the two resonances attributed to the methylene protons of the platinacyclic ring would be observed if ring reversal was occurring.

eq. 2.10



However, even up to  $100^\circ\text{C}$  at 90 MHz two separate resonances were observed in the spectrum showing that the boat conformation was rigid in solution and indicating a high energy barrier to ring reversal. This is in contrast to 9,10-dihydroanthracene itself, where n.m.r. studies show that ring reversal is rapid even at  $-100^\circ\text{C}$  at 100 MHz.<sup>260</sup> From the above observations a minimum value of the free energy of ring reversal  $\Delta G^\ddagger$  can be calculated to be  $70\text{ kJ mol}^{-1}$ .<sup>272</sup>



## 2.6.2 X-Ray Crystal Structure of $[(\text{PtEt}_3)_2 \text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

Selected bond lengths and angles are listed in Table 2.12 and information on angles and deviations from planes in Table 2.13. The numbering scheme for the molecule is shown in Fig. 2.24.

In compound (2.20e) the square planar geometry around the platinum atom is slightly distorted.

The six membered ring containing the platinum atom adopts a boat conformation as shown in Fig. 2.24. The atoms C(11), C(12), C(13) and C(14) are coplanar (plane 1) with both the platinum atom 1.16 Å and C(10) 0.67 Å above this plane. Assuming this boat conformation is maintained in solution the n.m.r. studies show that the ring is rigid at ambient temperature.

The platina-cyclic ring adopts a boat conformation because the molecule cannot be planar unless all the internal angles of the ring are 120°. This would introduce a high degree of angle strain and so the molecule folds about the Pt-C(10) axis.

The aromatic rings defined by [C(1), C(2), C(3), C(4), C(5), C(11)] (plane 2) and [C(5), C(6), C(7), C(8), C(14), C(13)] (plane 3) are inclined at an angle of 74.7°. The plane [Pt, C(10), C(11), C(12)] (plane 4) is at an angle of 69.5° to the plane [Pt, C(10), C(14), C(13)] (plane 5). The molecule thus consists of two separate halves hinged about the axis Pt-C(10) (dihedral angle 110.5°). However neither planes 1 and 3 nor planes 2 and 4 are coplanar. The trigonal geometries around C(12) and C(13) are distorted. The angles Pt-C(12)-C(8) and Pt-C(13)-C(1) are 127.4 (8)° and 127.5 (8)° respectively.

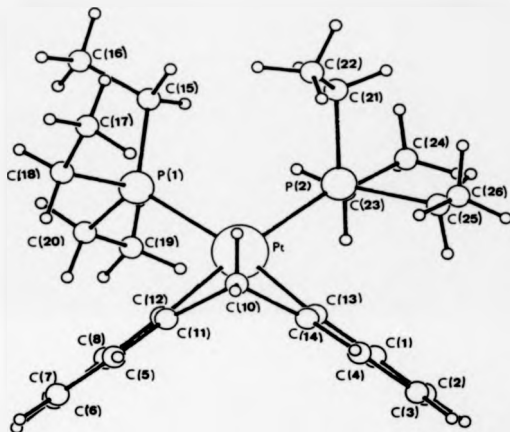


Fig. 2.24. An end on view of the platinumacyclic ring in molecule

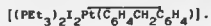
$[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  showing the atomic numbering scheme.

Table 2.12. Bond distances (Å) and bond angles (°) for  $[(\text{Pr}_3\text{C})_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4]$  (2.20a).

Bond distances (Å)			
Pr(1)-Pr(1)	2.323 (3)	Pr(1)-Pr(2)	2.303 (3)
Pr(1)-C(12)	2.062 (11)	Pr(1)-C(13)	2.038 (11)
Pr(1)-C(15)	1.801 (11)	Pr(1)-C(17)	1.799 (13)
Pr(1)-C(19)	1.810 (12)	Pr(2)-C(21)	1.835 (13)
Pr(2)-C(23)	1.797 (15)	Pr(2)-C(25)	1.825 (11)
C(12)-C(8)	1.378 (17)	C(12)-C(11)	1.364 (15)
C(8)-C(7)	1.384 (18)	C(7)-C(6)	1.355 (19)
C(6)-C(5)	1.360 (19)	C(5)-C(11)	1.382 (17)
C(11)-C(10)	1.531 (17)	C(10)-C(14)	1.512 (14)
C(14)-C(4)	1.348 (17)	C(14)-C(13)	1.415 (15)
C(4)-C(3)	1.374 (20)	C(3)-C(2)	1.363 (19)
C(2)-C(1)	1.380 (18)	C(1)-C(13)	1.399 (15)
C(15)-C(16)	1.523 (20)	C(17)-C(18)	1.510 (19)
C(19)-C(20)	1.498 (16)	C(21)-C(22)	1.478 (22)
C(23)-C(24)	1.500 (23)	C(25)-C(26)	1.591 (16)



Table 2.15. Deviations (Å) from mean planes (defined by starred atoms; e.s.d.s.  $\pm 0.005$  Å) in



## Plane 1

Pt	1.164	*C(13)	0.007	*C(14)	0.008
C(10)	0.678	*C(11)	0.008	*C(12)	0.007

## Plane 2

*C(1)	0.011	*C(2)	0.009	*C(3)	0.007
*C(4)	0.165	*C(14)	0.036	*C(13)	0.033

## Plane 3

*C(5)	0.008	*C(6)	0.027	*C(7)	0.019
*C(8)	0.007	*C(12)	0.025	*C(11)	0.017

## Plane 4

*Pt	0.021	*C(10)	0.029	*C(11)	0.058
*C(12)	0.058				

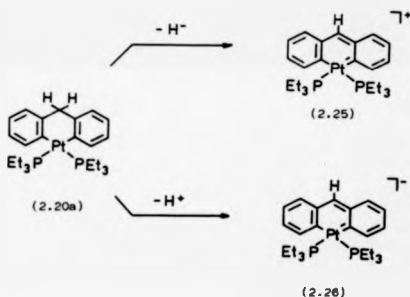
## Plane 5

*Pt	0.018	*C(10)	0.024	*C(14)	0.048
C(13)	0.042				

The dihedral angle of  $110.5^\circ$  signifies a large degree of ring folding and indicates that the boat conformation is highly puckered. It is the smallest dihedral angle reported for a 9,10-dihydroanthracene compound.

## 2.7 ATTEMPTED AROMATISATION OF $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

The compound  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20a) was treated with a series of reagents in an attempt to remove either  $\text{H}^+$  or  $\text{H}^-$  from the  $\text{sp}^3$  hybridised carbon with subsequent formation of a fully delocalised heteroanthracene compound (2.25) or (2.26) (Scheme 2.5).



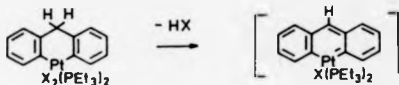
Scheme 2.5. Attempted aromatization of (2.20a) by removal of either  $\text{H}^+$  or  $\text{H}^-$ .

Compound (2.20a) was treated with the bases methylolithium, butyllithium, tert-butyllithium and lithium bis(trimethylsilyl) amide in an attempt to remove  $H^+$ , and with the reagent trityltetrafluoroborate in an attempt to remove  $H^-$ . All the reactions were followed by  $^1H$  n.m.r. and  $^{31}P\{-^1H\}$  n.m.r. spectroscopy. However, even additions of up to 10 mole equivalents of each of the above reagents and leaving the solutions for several hours or days did not result in the desired product being formed. In all cases only decomposition to other platinum containing species was observed to occur.

In the  $^1H$  n.m.r. spectrum, one of the resonances due to the two methylene protons would be expected to disappear as loss of either  $H^+$  or  $H^-$  occurred. The  $^{31}P\{-^1H\}$  n.m.r. spectrum would be expected to change significantly since removal of either  $H^+$  or  $H^-$  would cause a change in the bonding involved between the platinum and the 9,10-dihydroanthracene moiety. This would indirectly affect the  $^{31}P$  chemical shift and  $^1J(PtP)$  values which are very sensitive to the nature of the bonding of the ligand trans to the phosphorus nuclei.<sup>271</sup>

Since abstraction of either  $H^+$  or  $H^-$  from the platinum(II) complex (2.20a) was not successful, it was reasoned that loss of  $HX$  from a platinum(IV) complex such as  $[(PEt_3)_2X_2Pt(C_6H_4CH_2C_6H_4)]$  (2.27) would be more energetically favourable (eq. 2.11).

eq. 2.11

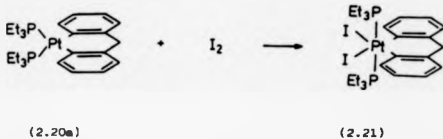


(2.27)

2.8 SYNTHESIS AND CHARACTERISATION OF  $[(\text{PET}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$   
and  $[(\text{dppm})\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

Several attempts at oxidative addition to the platinum(II) complex (2.20a) with substances such as methyl iodide, acetyl chloride and allyl chloride were unsuccessful. No reaction was observed with acetyl chloride and allyl chloride whilst reaction with methyl iodide gave  $[\text{PtI}_2(\text{PET}_3)_2]$  as evidenced by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy. However addition of one equivalent of iodine to compound (2.20a) produced the desired platinum(IV) complex (2.21) (eq. 2.12).

eq. 2.12



The addition required several hours since a build up in the local concentration of the iodine resulted in the formation of  $[\text{PtI}_2(\text{PET}_3)_2]$  resulting from reductive elimination. A slight excess of iodine also resulted in contamination of the product with this complex. The platinum(IV) compound (2.21) was isolated as a bright yellow, air-stable, crystalline solid which was characterised by  $^1\text{H}$ ,  $^{31}\text{P}$ - $^1\text{H}$ ,  $^{13}\text{C}$ - $^1\text{H}$  and  $^{195}\text{Pt}$ - $^1\text{H}$  n.m.r. spectroscopy and elemental analysis.



The elemental analysis of compound (2.21) did indicate that oxidative addition of iodine to the compound (2.20a) had occurred. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of compound (2.21) (data given in Table 2.10) showed that the triethylphosphine ligands were in a trans arrangement with the two incoming iodide ligands mutually cis. If the phosphine ligands had remained mutually cis, and trans to the 9,10-dihydroanthracene moiety on oxidative addition of iodine, the  $^1\text{P}(\text{PtP})$  value in the resulting platinum(IV) complex would be expected to be ca two thirds the magnitude of the value of the coupling constant in the platinum(II) complex<sup>278</sup> (i.e. ca 1200 Hz). The observed  $^1\text{J}(\text{PtP})$  value of 1782 Hz indicates that the phosphine ligands have rearranged so they are trans to each other. Phosphines have a lower trans influence than the 9,10-dihydroanthracene ligand and so this results in the higher coupling constant.

The  $^1\text{H}$  n.m.r. spectrum of (2.21) (Fig. 2.25, data given in Table 2.9) showed a single resonance for the two methylene protons of the 9,10-dihydroanthracene ligand signifying that the six membered platinacycle was undergoing rapid ring reversal on the n.m.r. timescale at ambient temperature. Therefore oxidative addition of iodine to compound (2.20a) has decreased the activation energy required for ring reversal.

Since the conformation of the platinacyclic ring was no longer rigid in solution only one resonance was observed for the methylene protons of the triethylphosphine ligands.

An interesting feature in the  $^1\text{H}$  n.m.r. spectrum of (2.21) was the presence of a resonance at lower field than the other

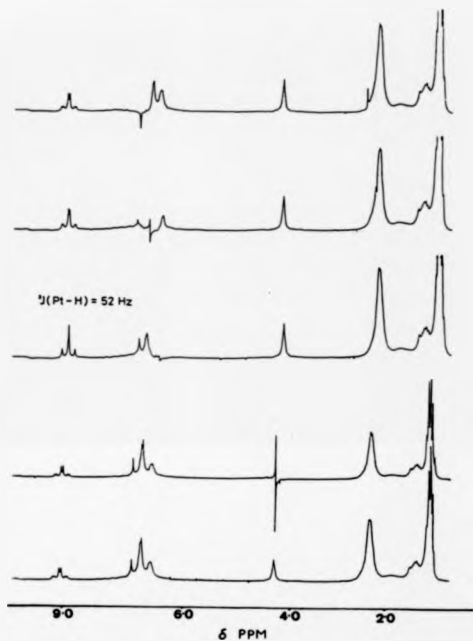
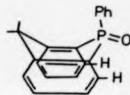


Fig. 2.25.  $^1\text{H}$  n.m.r. spectra ( $\text{CDCl}_3$ , 180 MHz) of  
 $[(\text{PEt}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  showing selective proton  
 decoupling.

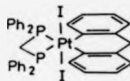
aromatic proton resonances (see Fig. 2.25). The resonance showed coupling to one other proton and had platinum satellites [ $^3J(\text{PtH}) = 52 \text{ Hz}$ ]. Proton decoupling studies (Fig. 2.25) enabled assignment of this resonance to the protons on C(1) and C(8) of the aromatic groups in the 9,10-dihydroanthracene moiety. It is thought that these two protons are deshielded by either the platinum atom or the two iodine ligands by a through space effect. Such an effect is seen in compound (2.28) where the aromatic protons ortho to the rigidly held P=O group are deshielded and well separated from the other aromatic protons. The close proximity of these protons to the equatorial phosphinoyl oxygen atom gives rise to this effect.<sup>279</sup>



(2.28)

Oxidative addition of iodine to the dppm complex (2.20g) was followed by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of the product in solution was consistent with the formation of the platinum(IV) complex (2.22) [ $\delta^{31}\text{P} = 31.0 \text{ ppm}$ ,  $^1J(\text{PtP}) = 954 \text{ Hz}$ ]. The dppm ligand is chelating, and hence the two iodine ligands are trans to each other. The  $^1J(\text{PtP})$  coupling constant [ $J(\text{PtP}) = 954 \text{ Hz}$ ] in the product is approximately two

thirds the value found in the platinum(II) complex [ $^1J(\text{PtP}) = 1466$  Hz] which would be expected if the iodine ligands were in the trans positions.



(2.22)

## 2.9 CONFORMATIONAL STUDIES OF $[(\text{PhC}_6\text{H}_4)_2\text{P}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

### 2.9.1 Solution N.M.R. Studies of $[(\text{PhC}_6\text{H}_4)_2\text{P}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

The crystal structure of compound (2.21) (Section 2.9.2) showed that if the boat conformation of the platinumacyclic ring was rigid in solution, the two phosphine ligands would not be chemically equivalent. One phosphine ligand would be above the boat and one would be below it. Hence two signals would be observed in the  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectrum. This prompted variable low temperature  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. studies of compound (2.21). Fig. 2.26 shows that as the temperature is lowered the phosphine ligands are rendered inequivalent as indicated by the presence of two signals in the spectrum. Only a small chemical shift difference is observed but readily detected at high field (162 MHz). The lack of solubility of the compound (2.21) in the solvent was observed at  $-100^\circ\text{C}$ .

On inspection of Fig. 2.26 it can be seen that at  $-95^{\circ}\text{C}$  the two phosphorus signals are nearly fully resolved and so an approximate value for the rate of ring reversal can be obtained at the coalescence temperature  $T_c$ , if the slow exchange limit is taken to be at the temperature  $-95^{\circ}\text{C}$ .

At  $T_c$ , the rate constant for ring inversion

$$k_c = \frac{1}{\tau}$$

where

$$\tau = \frac{\sqrt{2}}{\pi \nu_{AB}}$$

and  $\nu_{AB}$  is the frequency difference between the two phosphorus signals at the slow exchange limit.<sup>280</sup>

At the approximate slow exchange limit temperature  $-95^{\circ}\text{C}$  the two phosphorus nuclei have chemical shift values (162 MHz) of  $-2905.79$  Hz and  $-2924.60$  Hz with  $^1\text{J}(\text{PtP})$  coupling constants of 1734 Hz and 1779 Hz respectively.

The coalescence temperature  $T_c$  is estimated to be 195 K. Using the data obtained from the low temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. studies the rate of ring reversal in (2.21) at  $T_c = 195$  K is calculated to be ca  $42 \text{ s}^{-1}$ . An error of  $\pm 2$  Hz in  $\nu_{AB}$  would introduce an error of  $\pm 4 \text{ s}^{-1}$  into the above rate constant. Assuming  $\nu_{AB}$  is 18.8 Hz and 195 K the temperature of coalescence  $T_c$ , a value of  $\Delta G^\ddagger = 40.9 \text{ kJ mol}^{-1}$  (eq. 2.13)<sup>272</sup> is obtained for the free energy of activation associated with the ring reversal.

$$\Delta G^\ddagger = 19.12 T_c [9.97 + \log (T_c / \nu_{AB})]$$

eq. 2.13

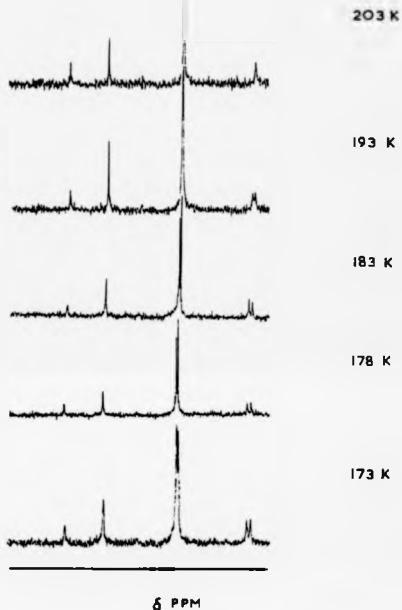


Fig. 2.26. Low temperature  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectra

( $\text{CH}_2\text{Cl}_2$ , 162 MHz) of  $[(\text{PEt}_3)_2\text{I}_2\text{Fe}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$ .

Alternatively, the frequencies of the  $^{195}\text{Pt}$  satellites can be used to calculate  $\Delta G^\ddagger$  for ring inversion. If  $-95^\circ\text{C}$  is taken to be the slow exchange limit  $\nu_{\text{AB}}$  is calculated to be 44.5 Hz. Taking 201 K as the temperature of coalescence, a value of  $\Delta G^\ddagger = 40.8 \text{ kJ mol}^{-1}$  is obtained.

An error in the coalescence temperature  $T_c$  of  $\sim 2 \text{ K}$  would introduce an error of  $0.4 \text{ kJ mol}^{-1}$  into the value of  $\Delta G_{T_c}^\ddagger$ . Similarly an error in the  $\nu_{\text{AB}}$  by  $\sim 4 \text{ Hz}$  would introduce an error of  $0.4 \text{ kJ mol}^{-1}$ . Hence a reasonable value of  $\Delta G_{T_c}^\ddagger = 40.9 \pm 0.4 \text{ kJ mol}^{-1}$  is obtained for the free energy of activation associated with ring reversal in the platinum(IV) compound  $[(\text{PET}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.21).

## 2.9.2 X-Ray Crystal Structure of $[(\text{PET}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

Selected bond lengths and angles are listed in Table 2.14 and information on angles and deviations from planes in Table 2.15. The numbering scheme for the molecule is shown in Fig. 2.27.

In the platinum(IV) compound (2.21) the octahedral geometry around the platinum atom is slightly distorted. It can be seen from Fig. 2.27 that the two iodine ligands are mutually cis and the two triethylphosphine ligands are trans to each other.

The conformation of the six membered platinacyclic ring is also a boat, where both the platinum atom ( $0.45 \text{ \AA}$ ) and C(10) ( $0.40 \text{ \AA}$ ) lie above the mean plane defined by C(11), C(12), C(13), C(14) (plane 1). The displacement of the platinum atom from this plane has decreased in compound (2.21) compared to the platinum(II) compound (2.20a) as a result of flattening of the boat conformation.

In compound (2.21) the aromatic rings defined by [C(1), C(2), C(3), C(4), C(12), C(11)] (plane 2) and [C(5), C(6), C(7), C(8), C(14), C(13)] (plane 3) are inclined at an angle of 28.8°. The plane [Pt, C(11), C(12), C(10)] (plane 4) is at an angle of 33.7° to the plane [(Pt, C(14), C(13), C(10))] (plane 5). The trigonal geometries around C(12) and C(13) are again distorted. The angles Pt-C(12)-C(11) and Pt-C(13)-C(14) are 123.1 (13)° and 122.6 (11)° respectively.

The flattening of the boat conformation of the platinacyclic ring can be seen in Fig. 2.27 and on inspection of the dihedral angle of 146.3°. This value is comparable to the dihedral angle of 145° in 9,10-dihydroanthracene<sup>231</sup>. It signifies a flattening of the tricyclic system. A dihedral angle of 180° indicates a completely planar molecule.

2.10 ATTEMPTED AROMATISATION OF  $[(\text{PEt}_3)_2\text{I}_2 \text{Pt}(\overline{\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4})]$  and  $[\text{dppm}]\text{I}_2 \text{Pt}(\overline{\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4})$ .

For delocalisation of electrons to occur following removal of a proton from the methylene carbon atom C(10) of the 9,10-dihydroanthracene moiety in  $[(\text{PEt}_3)_2\text{I}_2 \text{Pt}(\overline{\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4})]$  (2.21), necessitates the two aromatic rings of the 9,10-dihydroanthracene moiety moving into the plane of the ring defined by [C(11), C(12), C(13), C(14)]. The X-ray crystal structure shows that the aromatic rings are not far displaced from this plane in the platinum(IV) compound  $[(\text{PEt}_3)_2\text{I}_2 \text{Pt}(\overline{\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4})]$  (2.21) and hence it was reasoned that removal of a proton from (2.21) would be possible. Another indication that this may be so is that ring



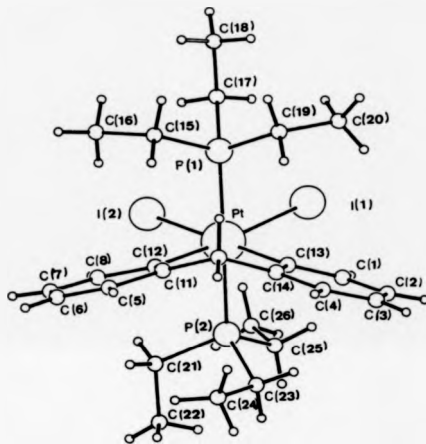
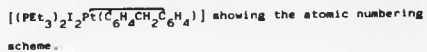


Fig. 2.27. An end on view of the platina-cyclic ring in the molecule



**Table 2.14.** Bond distances (Å) and bond angles (°) for  $[(\text{Prf}_3)_2\text{Pr}(\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_4)](2.21)$ .

Bond distances (Å)	
Pr(1)-I(1)	2.755 (10)
Pr(1)-Pr(1)	2.381 (3)
Pr(1)-C(12)	2.093 (15)
Pr(1)-C(15)	1.817 (19)
Pr(1)-C(19)	1.826 (16)
Pr(2)-C(23)	1.837 (17)
C(12)-C(8)	1.366 (26)
C(8)-C(7)	1.381 (24)
C(6)-C(5)	1.327 (20)
C(11)-C(10)	1.533 (27)
C(14)-C(4)	1.502 (25)
C(4)-C(3)	1.346 (27)
C(2)-C(1)	1.426 (24)
C(15)-C(16)	1.490 (28)
C(19)-C(20)	1.535 (28)
C(23)-C(24)	1.528 (24)
Pr(1)-I(2)	2.814 (10)
Pr(1)-Pr(2)	2.391 (3)
Pr(1)-C(13)	2.078 (14)
Pr(1)-C(17)	1.804 (15)
Pr(2)-C(25)	1.821 (16)
Pr(2)-C(29)	1.821 (19)
C(12)-C(11)	1.390 (17)
C(7)-C(6)	1.368 (23)
C(5)-C(11)	1.415 (26)
C(10)-C(14)	1.469 (22)
C(3)-C(13)	1.424 (17)
C(3)-C(2)	1.328 (23)
C(1)-C(13)	1.426 (21)
C(17)-C(18)	1.496 (19)
C(21)-C(22)	1.544 (20)
C(25)-C(26)	1.614 (25)

Table 2.14 (continued)

Bond angle [°]		
I(1)-Pt(1)-I(2)	81.9 (10)	I(1)-Pt(1)-P(1)
I(2)-Pt(1)-I(1)	87.4 (10)	I(1)-Pt(1)-P(2)
I(2)-Pt(1)-I(2)	94.3 (10)	P(1)-Pt(1)-P(2)
I(1)-Pt(1)-I(2)	173.2 (4)	I(2)-Pt(1)-C(12)
P(1)-Pt(1)-C(12)	92.7 (3)	P(2)-Pt(1)-C(12)
I(1)-Pt(1)-C(13)	94.0 (4)	I(2)-Pt(1)-C(13)
P(1)-Pt(1)-C(13)	90.7 (3)	P(2)-Pt(1)-C(13)
C(12)-Pt(1)-C(13)	91.9 (6)	Pt(1)-P(1)-C(15)
Pt(1)-P(1)-C(17)	116.1 (4)	C(15)-P(1)-C(17)
Pt(1)-P(1)-C(19)	115.1 (6)	C(15)-P(1)-C(19)
C(17)-P(1)-C(19)	104.7 (7)	Pt(1)-P(2)-C(21)
Pt(1)-P(2)-C(23)	116.3 (4)	C(21)-P(2)-C(23)
Pt(1)-P(2)-C(25)	115.5 (4)	C(21)-P(2)-C(25)
C(23)-P(2)-C(25)	98.9 (8)	Pt(1)-C(12)-C(6)
Pt(1)-C(12)-C(11)	123.1 (13)	C(6)-C(12)-C(11)
C(12)-C(6)-C(15)	121.9 (14)	C(6)-C(5)-C(11)
C(7)-C(6)-C(15)	118.4 (18)	C(12)-C(11)-C(10)
C(12)-C(11)-C(5)	119.2 (17)	C(11)-C(10)-C(14)
C(5)-C(11)-C(10)	116.4 (12)	C(10)-C(14)-C(13)
C(10)-C(14)-C(13)	119.3 (12)	C(14)-C(4)-C(3)
C(4)-C(14)-C(13)	116.1 (14)	C(3)-C(2)-C(1)
C(2)-C(1)-C(13)	119.1 (17)	Pt(1)-C(13)-C(14)
C(1)-C(13)-C(11)	122.5 (12)	C(14)-C(13)-C(1)
Pt(1)-C(13)-C(11)	120.5 (9)	P(1)-C(17)-C(18)
P(1)-C(17)-C(18)	118.2 (10)	P(2)-C(21)-C(22)
C(1)-C(19)-C(20)	115.7 (10)	P(2)-C(25)-C(26)
P(2)-C(25)-C(26)	114.8 (14)	
		90.6 (10)
		90.3 (10)
		178.2 (10)
		92.1 (4)
		86.6 (3)
		175.5 (4)
		87.6 (3)
		101.4 (8)
		116.1 (4)
		101.5 (6)
		115.8 (6)
		102.8 (7)
		105.3 (6)
		119.2 (10)
		117.5 (15)
		120.6 (17)
		122.3 (15)
		124.1 (15)
		117.8 (11)
		124.6 (14)
		124.0 (13)
		121.4 (16)
		122.6 (11)
		116.7 (13)
		116.1 (10)
		114.3 (14)
		116.1 (16)

Table 2.13. Deviations (Å) from mean planes (defined by starred atoms; s.e.d.s.  $\pm 0.005$  Å) in  $[(\text{Pt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

## Plane 1

Pt	0.454	C(10)	0.407	*C(11)	0.248
*C(12)	0.021	*C(13)	0.020	*C(14)	0.240

## Plane 2

*C(1)	0.012	*C(2)	0.022	*C(3)	0.010
*C(4)	0.011	*C(14)	0.018	*C(13)	0.007

## Plane 3

*C(5)	0.002	*C(6)	0.003	*C(7)	0.008
*C(8)	0.018	*C(12)	0.018	*C(11)	0.008

## Plane 4

*Pt	0.013	*C(10)	0.018	*C(11)	0.040
*C(12)	0.035				

## Plane 5

*Pt	0.000	*C(10)	0.000	*C(14)	0.001
*C(13)	0.001				

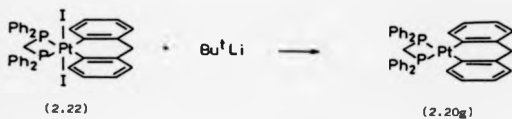
reversal in (2.21) is rapid in solution on the n.m.r. timescale at ambient temperature. The transition state for this process is most likely to be when the aromatic rings are in this plane, i.e. when the steric interactions between the peri protons on the 9,10-dihydroanthracene ligand and the two iodine ligands are at a maximum. If the transition state for ring reversal is planar, all the internal angles of the platinacyclic ring would approximate to  $120^\circ$ . This would introduce a considerable degree of angle strain. However, the fact that ring reversal does occur suggests that the steric interactions and angle strain (which would also be encountered in the delocalised ('platinanthracene' moiety) can be accommodated in the molecule. It was also reasoned that reductive elimination of HI from compound (2.21) would be energetically favourable.

Compound (2.21) was treated with a series of bases and the reactions followed by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy. Treatment of (2.21) with triethylamine even in large excess showed no change in the  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectrum. Reaction of (2.21) with tert-butyllithium gave a clean  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectrum containing only one species, which was consistent with reductive elimination of iodine to give the platinum(II) compound (2.20a). Reaction of aliquots of the base lithium bis(trimethylsilyl)amide with (2.21) resulted in decomposition of (2.21) to give a number of platinum containing species including cis and trans  $[(\text{PET})_2 \text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)\text{I}]$  and cis and trans  $[\text{PtI}_2(\text{PET})_2]$

Treatment of  $[(\text{dppm})\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.22) with aliquots of the base tert-butyllithium was followed by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r.

spectroscopy. It was possible that a competing reaction may be abstraction of a proton from the methylene group of the dpdm ligand instead of the proton from C(10) in the 9,10-dihydroanthracene moiety. However, the only reaction observed to occur as evidenced by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy was reductive elimination of iodine to give the platinum(II) compound (2.20g) (eq. 2.14).

eq. 2.14



## 2.11 DISCUSSION

### 2.11.1 Conformational Studies of $[(\text{Ph}_2\text{P})_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$ and $[(\text{Ph}_2\text{P})_2\text{Pt}_2(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$

It is clear from the X-ray crystal structures that the six membered platinacyclic rings in the platinum(II) and platinum(IV) compounds, (2.20a) and (2.21) respectively, both adopt a boat conformation. However the platinacyclic ring in the platinum(IV) compound (2.21) is flattened in comparison to the ring in the platinum(II) compound (2.20a). This is seen on inspection of the dihedral angle of fold in the two compounds which is  $110.5^\circ$  in (2.20a) and  $146.5^\circ$  in (2.21).

The flattening of the platinacyclic ring in the platinum(IV) compound (2.21) is a result of the presence of the triethylphosphine ligands above and below the platinacyclic ring. However it is not immediately clear why the phosphine ligands should rearrange to the trans positions on oxidative addition of iodine. Possibly the electronic effects are more favourable in the resulting isomer than any of the other possible isomers or it may be that steric interactions between the *peri* protons on the aromatic rings of the 9,10-dihydroanthracene moiety are minimized when the iodine ligands are trans to it. A consequence of this would be that the aromatic rings could move more into the plane [C(11), C(12), C(13), C(14)] of the ring, before steric interactions become unfavourable. This is certainly the case where the aromatic rings defined by the mean planes [C(1), C(2), C(3), C(4), C(14), C(13)] and [C(5), C(6), C(7), C(8), C(12), C(11)] are now at angles of 13.4° and 15.7° respectively to the plane defined by [C(11), C(23), C(13), C(14)]. In the platinum(II) compound (2.20a) the corresponding angles are 37.3° and 37.4°.

The flattening of the boat conformation of the platinacyclic ring in the platinum(IV) compound (2.21) explains the much lower energy barrier to ring reversal detected in solution n.m.r. studies. In the platinum(IV) compound (2.21) rapid ring reversal occurs on the n.m.r. timescale at ambient temperature. This is in sharp contrast to (2.20a) where even at 100 °C the boat conformation is rigid in solution. The difference in the energy barriers to ring reversal for compounds (2.20a) and (2.21) originates from differences in energy of both the ground states and transition states for the process.

### 2.11.2 Saturated and Unsaturated Six Membered Platinacycles

It is interesting to compare the effect of replacement of a methylene group in cyclohexane and 9,10-dihydroanthracene with a square planar platinum atom. In the saturated platinacycle (2.16b) the platinum has resulted in flattening of the chair conformation and led to a decrease in the energy barrier to ring reversal. Even at  $-150^{\circ}\text{C}$  at 400 MHz the ring in (2.16a) undergoes rapid ring reversal. In contrast, the effect of the platinum atom on the conformation of 9,10-dihydroanthracene is to increase the puckering of the boat conformation of the central ring and to raise the energy barrier to ring reversal. At  $100^{\circ}\text{C}$  and 400 MHz the boat conformation in (2.20a) was rigid in solution. The conformations adopted by the platinacyclic rings result from a balance of both angle strain due to the smaller C-Pt-C bond angles and steric effects imposed by the square planar geometry of the platinum atom.

### 2.11.3 Attempted Aromatization

Attempts to obtain a 'platinaanthracene' moiety by abstraction of either  $\text{H}^{\bullet}$  or  $\text{M}^{-}$  from the platinum(II) compound  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (2.20a) were unsuccessful. However in view of the conformational studies carried out on (2.20a) it is perhaps not surprising. If either  $\text{H}^{\bullet}$  or  $\text{M}^{-}$  abstraction was to occur, the aromatic rings of the 9,10-dihydroanthracene moiety and the square planar platinum(II) atom would be required to move into the plane [C(11), C(12), C(13), C(14)], for electron delocalisation to occur. This would not only introduce angle strain effects in having all the atoms coplanar but would require the triethylphosphine ligands



to move into the same plane as the peri protons on the aromatic rings. This would result in a considerable degree of unfavourable steric interaction which it would appear cannot be accommodated in a ground state molecule such as the 'platinaanthracene' moiety.

The inability to abstract a proton from the platinum(IV) compound (2.21), by reductive elimination of HI to form a 'platinaanthracene' moiety was disappointing, considering the X-ray crystal structure showed that the platinacyclic ring was flattened and the  $^1\text{H}$  n.m.r. studies indicated rapid ring reversal was occurring on the n.m.r. timescale at ambient temperatures.

An important factor in the unsuccessful attempts to obtain a 'platinaanthracene' moiety was the competing reaction of reductive elimination of  $\text{I}_2$  from the platinum(IV) compound. It is possible that oxidative addition of other substrates or use of smaller ligands than phosphines would lead to the successful synthesis of platinaanthracenes.

## CHAPTER THREE

SIX MEMBERED CHELATE STABILISED ALCOHOL- AND ALKOXO-  
PLATINUM(II) AND PALLADIUM(II) COMPLEXES

## 3.1 INTRODUCTION

Complexes of the late transition metals containing weak donor ligands which may be readily displaced by a substrate molecule have been used to obtain catalytic activity in transformations involving unsaturated organic substrates.<sup>281,282</sup> In recent years transition metal complexes containing bidentate ligands which have one strong and one weak donor group, have been studied.<sup>283,284</sup> Such compounds may be useful as homogenous catalysts.<sup>285</sup> The chelate effect confers additional stability on the complex in the absence of the substrate whilst the weak donor retains its susceptibility to displacement by a substrate molecule.

An example of an unsymmetrical, potentially bidentate ligand is the functionalised phosphine containing one diphenylphosphine and one alcohol (3.1a) or ether (3.1b) group. These ligands form five membered chelates with platinum(II).<sup>286-289</sup>



(3.1a)      R=H

(3.1b)      R=CH<sub>3</sub>

In the present work the functionalised phosphine ligand (3.2) was synthesised in an attempt to obtain six membered chelate-stabilised alcohol- or alkoxo- platinum(II) complexes.



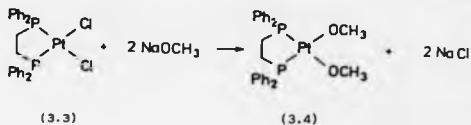
(3.2)

### 3.1.1 Monodentate Oxygen Donor Complexes of Platinum

Hard ligands containing the electronegative oxygen donor atom would be expected to bind only very weakly to the soft Lewis acid, platinum(II).<sup>290</sup> Oxygen donor complexes of the Group VIII (8-10) transition metals either (i) have several hard donors coordinated to the metal, a manifestation of the symbiotic effect,<sup>291</sup> or (ii) the oxygen donor is trans to a ligand of high trans influence such as hydride, alkyl or aryl ligands where the antisymbiotic effect promotes coordination.<sup>292</sup>

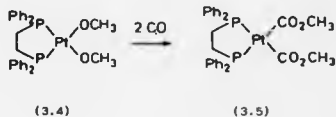
Well characterised alkoxo-platinum complexes are rare and generally unstable.<sup>293-295</sup> Those complexes which have been isolated are often extremely moisture, oxygen and temperature sensitive. In 1986 the first well characterised but highly reactive bis-alkoxo platinum complex (3.4) was prepared by the metathesis reaction of the corresponding dichloride (3.3) with sodium methoxide (eq. 3.1).<sup>296</sup>

eq. 3.1



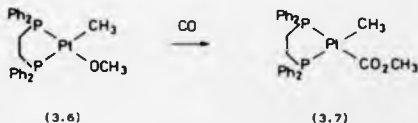
Complex (3.4) when treated with carbon monoxide, generated the stable bis-methoxy carbonyl product<sup>297</sup> (3.5) (eq. 3.2).

eq. 3.2



The highly reactive mono-alkoxy platinum complex (3.6) also undergoes carbon monoxide insertion to form the mono-methoxy carbonyl product (3.7) (eq. 3.3).

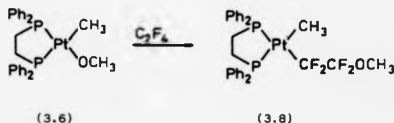
eq. 3.3



Insertion into the Pt-C bond in complex (3.6) was not observed although the insertion mechanism is analogous to those previously established for insertion into M-C bonds.<sup>298</sup>

Bryndza *et al.*<sup>299</sup> have shown that the previously unknown alkene insertion into a M-O bond can occur (eq. 3.4). Again, no insertion into the Pt-C bond was observed and the reaction proceeds

eq. 3.4

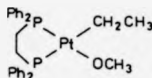


by the same mechanism as insertions into M-C and M-H bonds in which association of the alkene to give a five coordinate complex is followed by insertion into the Pt-O bond. It is interesting to note that in the above two insertion reactions, the hard base/soft acid complex (3.6) does not depend on dissociation of methoxide for reactivity.

The difficulty in isolating alkoxo complexes of the Group VIII (8-10) transition metals has been attributed to the commonly held perception that such species have weak M-O bonds due to the weak interaction of the hard base with the relatively soft Group VIII (8-10) metal centres.<sup>290</sup> The dominant decomposition pathway of metal alkoxides is  $\beta$ -hydrogen elimination and the ease with which metal alkoxides decompose to form metal hydrides has been assumed

to be due to the weak M-O bonds lowering the intrinsic barrier to  $\beta$ -hydrogen elimination reactions by raising the ground state free energies of alkoxides relative to alkyls.<sup>297</sup>

Bryndza *et al.*<sup>297</sup> have shown that decomposition of platinum(II) alkoxides is a low energy process but where both ethyl and methoxy ligands are present as in compound (3.9), decomposition from ethyl ligand  $\beta$ -elimination predominates.



(3.9)

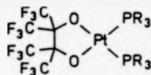
Thermodynamic studies on  $[(dppe)Pt(OMe)_2]$  and  $[(dppe)Pt(CH_2CH_3)_2]$  indicate that the presence of non-associating polar bonds such as methoxide can accelerate  $\beta$ -hydrogen elimination from both alkyl and alkoxo ligands. These results are inconsistent with the assumption that the metal-oxygen bonds are intrinsically thermodynamically weak. A recent study by Bryndza and Bercaw<sup>300</sup> has shown that metal oxygen bonds for the late transition metals are not weak thermodynamically. In fact  $L_nM-OH$  bonds are found to be generally stronger than  $L_nM-C(sp^1)$ ,  $L_nM-H$  or  $L_nM-N$  bonds although nitrogen ligands such as acetonitrile and pyridine are found to bind much more readily to the platinum group metals. It would appear that the lability of many platinum oxygen donor complexes is kinetic in origin, as a result of the existence of facile

decomposition pathways such as  $\beta$ -hydrogen elimination, rather than thermodynamic in origin.

The energy barriers to  $\beta$ -hydrogen elimination from alkyl and alkoxo ligands may be controlled by design of complexes with appropriate ligands. For example, incorporation of M-O bonds into chelate rings leads to inhibition of the  $\beta$ -hydrogen elimination decomposition pathway and consequently such compounds have greater chemical stability.<sup>286,287</sup>

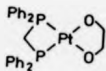
### 3.1.2 Chelate Stabilised Oxygen Donor Complexes of Platinum

Recently a number of platinum alkoxo complexes have been isolated where the Pt-O linkages have been incorporated into chelate rings. For example Willis *et al.*<sup>301</sup> have prepared stable fluoroalkoxides of platinum(II) using the bidentate perfluoro-pinacol dianion (3.10) with a range of phosphine co-ligands.



(3.10)

The chelating platinum alkoxo complexes have greater thermodynamic stability than the monodentate platinum alkoxides. The chelating glycolate platinum complex (3.11) on heating at 120 °C<sup>297</sup> for 3 days shows no signs of decomposition in contrast to the monodentate alkoxo complex (3.4) which is unstable even at room temperature.<sup>297</sup>



(3.11)

Pringle *et al.*,<sup>286,287</sup> have shown that the ligands  $\text{Ph}_2\text{PCH}_2\text{CMe}_2\text{OH}$  (3.12) and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OH}$  (3.13) form  $\sigma$ -donor complexes with platinum(II) which are air, moisture and thermally stable. They do not contain abnormally long or weak Pt-O bonds.



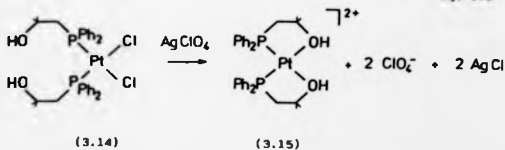
(3.12)



(3.13)

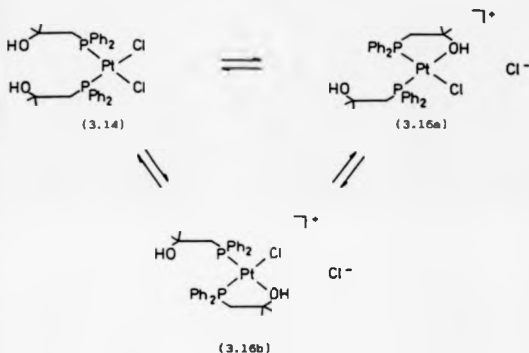
Reaction of the bis-phosphine complex (3.14) with  $\text{AgClO}_4$  gave the dicationic species (3.15) (eq. 3.5).

eq. 3.5





The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of the bis-phosphine complex (3.14) in  $\text{CDCl}_3$  is a broad singlet with  $^{195}\text{Pt}$  satellites which, when cooled to  $-40^\circ\text{C}$  sharpens to an AX pattern. The chelate complex (3.16) in which the alcohol donor is bonded to the metal was assigned to this species. The fluxionality in solution is due to interconversion of the tautomers (3.16a) and (3.16b) by rapid intramolecular  $-\text{OH}$  exchange as shown in Scheme 3.1.

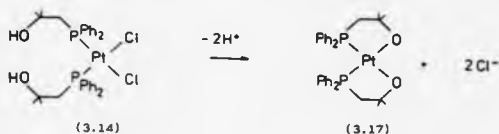


Scheme 3.1. Fluxional behaviour of  $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CMe}_2\text{OH})_2]$  in methanol.

Even in the absence of the silver salt the supposedly weak oxygen donor has displaced the chloro ligand.

Deprotonation of the bis-phosphine complex (3.14) with NaOH in ethanol,  $[\text{LiN}(\text{SiMe}_3)_2]$  in THF or  $\text{NEt}_3$  in  $\text{CDCl}_3$  gave the bis-alkoxo chelate complex (3.17) (eq. 3.6).

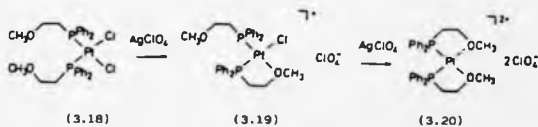
eq. 3.6



From the crystal structure of (3.17) it was deduced that the Pt-O bonds are the expected length for a single bond and show no anomalous weakening. The bis-alkoxo chelate complex (3.17) is air stable and can be refluxed in alcoholic KOH for 16 h without any sign of decomposition. This is in contrast to the mononuclear bis-alkoxoplatinum(II) complex  $[\text{Pt}(\text{OMe})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$  (3.4) which decomposes at  $25^\circ\text{C}$  in solution and is sensitive to water.

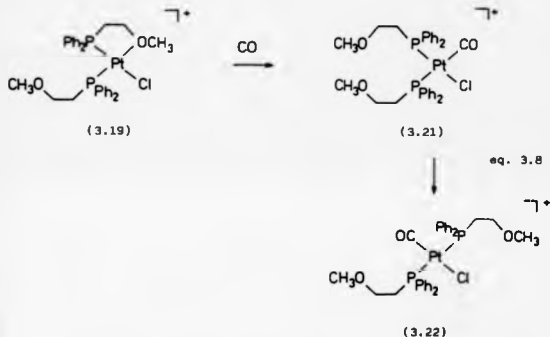
Anderson *et al.*<sup>288</sup> have shown that the chelate complexes (3.19) and (3.20) can be obtained from the functionalised phosphinoether  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe}$  (eq. 3.7).

eq. 3.7



From the crystal structure of the chelate ether complex<sup>289</sup> (3.19) it was found that the Pt-O bond length is 2.192(7) Å and is the longest platinum ether bond known. The Pt-O interaction is only formed when a vacant site is created by halide abstraction.

The reactivity of the Pt-O bond was investigated by treating complex (3.19) with carbon monoxide. The carbon monoxide molecule displaced the ether function, followed by isomerisation of the cis complex (3.21) to yield the trans complex (3.22) (eq. 3.8).

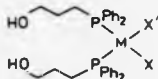


Reaction of complex (3.19) with pyridine or diethylsulphide resulted in displacement of the ether function but, in contrast to the reaction with CO, it is the cis isomer that is formed. No reaction with ethylene was observed. The stability of the complexes formed by Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OMe and the facile displacement of the ether

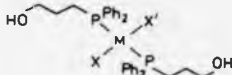
function in solution means that such complexes may prove useful as homogeneous catalysts.<sup>289</sup>

### 3.2 SYNTHESIS AND CHARACTERISATION OF PLATINUM (II) AND PALLADIUM(II) COMPLEXES OF $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH}$

Several bis-phosphine platinum(II) complexes of the type (3.23) and (3.24) were prepared and characterised, using the functionalised phosphine (3.2).

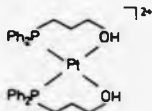


(3.23)

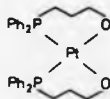


(3.24)

The six membered chelate-stabilised bis-alcohol complex (3.25) and bis-alkoxo complex (3.26) were also synthesised and the chemistry and reactions involving the Pt-O bonds investigated.



(3.25)



(3.26)

### 3.2.1 Synthesis and Characterisation of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH}$

The reported method<sup>302</sup> of synthesis of  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH}$  (3.2) involves ring opening of the cyclic ether trimethyleneoxide by treatment with lithium diphenylphosphide.

In the present work an alternative method using a more convenient starting material was used (eq. 3.9).

eq. 3.9



(3.2)

The phosphine was isolated as a white crystalline solid. It was handled for short periods in air during weighing etc. but was stored under an inert atmosphere to prevent oxidation. The phosphine was characterised by  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ - $^1\text{H}$  n.m.r. spectroscopy, infra-red spectroscopy and elemental analysis.

### 3.2.2 Synthesis and Characterisation of Bis-Phosphine Complexes of the Type $[\text{MCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$ (M=Pt or Pd)

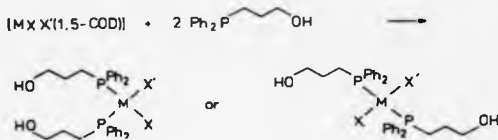
The bis-phosphine complexes (3.27a-d) and (3.28a-b) were prepared by reaction of the phosphine  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH}$  (3.2) with the appropriate metal complex as shown in eq. 3.10.

Table 3.1.  $^1\text{H}$  n.m.r. <sup>a</sup> data for compounds of the type  $[\text{MOC}(\text{R}_1\text{R}_2\text{C}^1\text{H}_2\text{C}^2\text{H}_2\text{C}^3\text{H}_2\text{C}^4\text{H}_2\text{OH})_2]$ .

Compound	$\delta\text{C}^1\text{H}_2$	multiplicity	$\delta\text{C}^2\text{H}_2$	multiplicity	$\delta\text{C}^3\text{H}_2$	multiplicity	$\delta\text{C}^4\text{H}_2$	multiplicity	Other proton Resonances
(3.27a)	1.84	br s	2.34	br m	3.47	m			7.26-7.64 (s)
(3.27b)	2.02	br m	2.56	br m	3.63	m			7.18-7.62 (s)
(3.27c)	2.92	br m	3.04	br m	3.72	m			7.30-7.82 (s)
(3.27d)	1.81	br m	1.91	br m	3.49	m			0.48 (s) J(PH) = 12.7 Hz, J(PP) = 69.9 Hz), 7.22-7.60 (s)
(3.28a)	1.94	br m	2.74	br m	3.84	m			0.08 (s) J(PH) = 13.7 Hz, J(PP) = 83.1 Hz), 7.38-7.78 (s)
(3.28b)	1.76	br m	2.55	br m	3.74	m			7.38-7.75 (s)
(3.25)	1.85	br d	2.64	m	4.26	m			7.28-7.68 (s)
(3.26)	1.82	br d	2.29	m	4.01	m			7.14-7.68 (s)

<sup>a</sup> Spectra (220 MHz) measured in methanol- $d_4$  at ambient temperature. Chemical shifts  $\delta$  in p.p.m. ( $\pm 0.01$ ) to highfrequency of  $\text{SiMe}_4$ . Coupling constants  $J$  in Hz ( $\pm 0.1$ )<sup>b</sup> Multiplicities: s = singlet, d = doublet, m = multiplet.

eq. 3.10



(3.27a) M=Pt, X=X'=Cl

(3.27b) M=Pt, X=X'=Br

(3.27c) M=Pt, X=X'=I

(3.27d) M=Pt, X=X'=CH<sub>3</sub>(3.28a) M=Pt, X=Cl, X'=CH<sub>3</sub>

(3.28b) M=Pd, X=X'=Cl

(3.28c) M=Pt, X=X'=I

All the complexes were isolated as air stable solids which were characterised by  $^1H$  and  $^{31}P$ - $(^1H)$  n.m.r. spectroscopy, infrared spectroscopy, and elemental analysis. The cis or trans assignments were made on the basis of the Pt-Cl stretching frequencies (data given in Table 3.1) and the  $J(PtP)$  coupling constants (data given in Table 3.1). The  $^1H$  n.m.r. spectra of compounds (3.27a-d) and (3.28a-b) (data given in Table 3.2) are similar. The  $^{31}P$ - $(^1H)$  n.m.r. spectra of complexes (3.27a-d) and (3.28a) and (3.28c) are singlet resonances with  $^{195}Pt$  satellites in each case.

At 25 °C the  $^{31}P$ - $(^1H)$  n.m.r. spectrum of cis- $[PtCl_2(Ph_2PCH_2CH_2CH_2OH)_2]$  (3.27a) in methanol is a broad singlet with  $^{195}Pt$  satellites. When the solution was cooled to -70 °C the

Table 3.2  $^{31}\text{P}$ - $^1\text{H}$  n.s.r.<sup>a</sup> and i.r.<sup>b</sup> data for compounds of the type  $[\text{MX}'(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$ .

Compound	$\delta(^{31}\text{P})$	$^1\text{J}(\text{PtP})$	cis/trans	(M-Cl)/cm <sup>-1</sup>
(3.27a)	7.2	3680	cis	285, 315
(3.27b)	9.0	3619	cis	-
(3.27c)	6.9	3495	cis	-
(3.28c)	3.8	2413	trans	-
(3.27d)	17.1	1873	cis	-
(3.28a)	22.3	3040	trans	275
(3.28b)	16.5	-	trans	355
(3.25)	-4.2	3924	cis	-
(3.26)	-5.3	3469	cis	-

<sup>a</sup> Spectra (162 MHz) measured in methanol at ambient temperature.

Chemical shifts  $\delta$  in ppm ( $\pm 0.1$ ) to high frequency of 85%  $\text{H}_3\text{PO}_4$ .

Coupling constants J in Hz ( $\pm 3$ ).

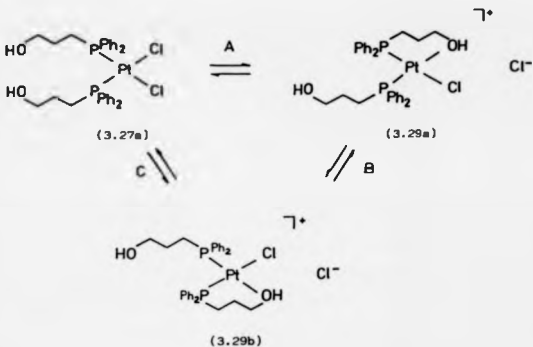
<sup>b</sup> Cesium iodide discs.



broad resonance sharpened. At ambient temperature, a solution of (3.27a) in methanol had a conductivity of  $860^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , suggesting an ionic species is present in solution, although the measurement is low for a 1:1 salt.

The low temperature  $^{31}\text{P}\text{--}(\text{H})$  n.m.r. observations are markedly different from the complex  $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OH})_2]$  (3.14) where the broad resonance obtained in methanol at  $25^\circ\text{C}$  sharpens to an AB pattern when cooled to  $-40^\circ\text{C}$ . The fluxionality of (3.14) was rationalized in terms of intramolecular  $\text{-OH}$  exchange (see Section 3.1.2).

One explanation for the observations made on (3.27a) is that at ambient temperature an exchange process A (Scheme 3.2) occurs involving the bis-phosphine complex (3.27a) and the chelate (3.29a) in which the alcohol is coordinating to the platinum(II) atom. If this is the case, addition of a  $\text{Cl}^-$  source would result in sharpening of the signal as the equilibrium A is shifted towards the bis-phosphine complex (3.27a). This is indeed what is observed on the addition of either  $\text{HCl}$  or  $[\text{PPN Cl}]$ . On cooling the solution the equilibrium position is changed so that again the bis-phosphine complex (3.30) alone is present in solution. This is in contrast to the observations of Pringle *et al.*<sup>287</sup> where methanol solutions of  $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OH})_2]$  (3.14) on cooling contained exclusively the monochelate (3.16).



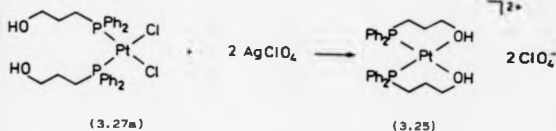
**Scheme 3.2.** Fluxional behaviour of  $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  in methanol.

### 3.3 SOME REACTIONS OF CIS-[PtCl<sub>2</sub>(Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>]

### 3.3.1 Reaction of *cis*-[PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] with AgClO<sub>4</sub>

Addition of two equivalents of  $\text{AgClO}_4$  to the bis-phosphine complex (3.27a) in methanol gives the cis-dicationic complex (3.25) in which the phosphine ligand is chelating and both the phosphorus and oxygen atoms are coordinated to the platinum(II) atom (eq. 3.11).

eq. 3.11



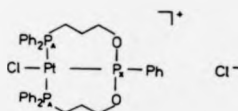
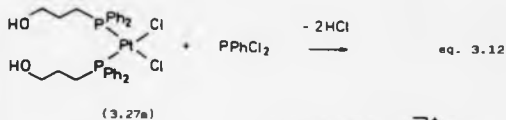
Complex (3.25) was isolated as a white air stable solid which was characterised by  $^1\text{H}$  and  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy, infra-red spectroscopy (absence of Pt-Cl bands) and elemental analysis. The large  $^1\text{J}(\text{PtP})$  of 3924 Hz (Table 3.2) is consistent with the trans alcohol group being a poor donor for the platinum(II).

### 3.3.2 Reaction of cis- $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OH})_2]$ with $\text{PPhCl}_2$

The -OH bonds in the bis-phosphine complex

$[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OH})_2]$  (3.27a) reacts with hydrolysable P-Cl bonds to form phosphonite type ligands. Addition of one equivalent of  $\text{PPhCl}_2$  to (3.27a) in chloroform gave one major species in solution,  $[\delta^{31}\text{P}_\text{X} \text{ } 119.9 \text{ p.p.m.}, ^1\text{J}(\text{PtP}_\text{X}) = 4534 \text{ Hz}, \delta \text{P}_\text{A} \text{ } 9.2 \text{ p.p.m.}, ^1(\text{PtP}_\text{A}) = 2278 \text{ Hz}, ^2\text{J}(\text{P}_\text{X}\text{P}_\text{A}) = 21 \text{ Hz}]$ . This is consistent with the structure (3.30) in solution (eq. 3.12).

Addition of  $\text{NEt}_3$  gave white fumes of triethylammonium chloride  $\text{HNEt}_3^+\text{Cl}^-$ . No change in the major species in solution was observed as shown by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy.



### 3.4 SYNTHESIS AND CHARACTERISATION OF THE BIS-ALKOXO CHELATE COMPLEXES OF PLATINUM(II) AND PALLADIUM(II).

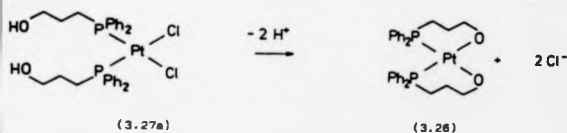
#### 3.4.1 Synthesis and Characterisation of $\text{cis-}[\text{Pt}(\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2)_2]$

The bis-phosphine complex (3.27a) is cleanly deprotonated by

$\text{NaOH}$  or  $\text{NEt}_3$  in methanol to give the bis-alkoxo chelate complex

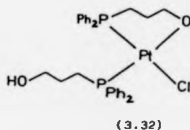
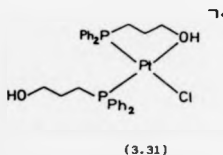
(3.26) (eq. 3.13).

eq. 3.13

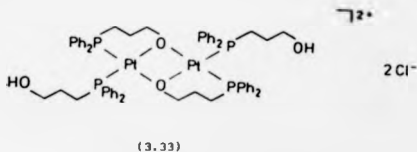


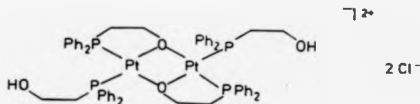
The bis-alkoxo chelate complex (3.26) was isolated as a white air stable solid and did not decompose on leaving solutions in methanol to stand for several hours (as shown by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy). Its structure was assigned on the basis of elemental analysis, infra-red spectroscopy (absence of Pt-Cl bands) and  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy. The  $^1\text{J}(\text{PtP})$  value in the bis-alkoxo chelate complex (3.26) (data given in Table 3.2) is ca 200 Hz lower than the coupling constant in the bis-phosphine complex cis- $[\text{PtCl}_2\text{P}_2]$  (3.27a) which suggests that the alkoxo group is a stronger  $\sigma$  donor for platinum than a chloro ligand.

Complex (3.27a) was titrated with aliquots of NaOH in methanol and the reaction followed by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy. The deprotonation appeared to involve several intermediate species. The  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectra of two of the intermediate species were similar showing an AB pattern with  $^{195}\text{Pt}$  satellites [ $\delta_{\text{P}_A}$  5.5 p.p.m.,  $^1\text{J}(\text{PtP}_A) = 3567$  Hz,  $\delta_{\text{P}_B}$  1.7 p.p.m.,  $^1\text{J}(\text{PtP}_B) = 3765$  Hz,  $^2\text{J}(\text{P}_A\text{P}_B) = 17$  Hz] and [ $\delta_{\text{P}_A}$  0.8 p.p.m.,  $^1\text{J}(\text{PtP}_A) = 3242$  Hz,  $\delta_{\text{P}_B}$  -7.5 p.p.m.,  $^1\text{J}(\text{PtP}_B) = 3441$  Hz,  $^2\text{J}(\text{P}_A\text{P}_B) = 18$  Hz]. The small  $^2\text{J}(\text{P}_A\text{P}_B)$  coupling constants in both cases are consistent with the phosphorus nuclei being mutually cis. It is not clear what structure these two species have but they may have structures similar to (3.31) and (3.32) although it would be expected that compound (3.31) would be fluxional in solution.



Deprotonation of the dichloro bis-phosphine complex (3.27a) with  $\text{NET}_3$  in methanol gave the same bis-alkoxo chelate complex (3.26). However addition of  $\text{NET}_3$  in chloroform to the dichloro complex (3.27a) gave a species whose  $^{31}\text{P}\text{-}({}^1\text{H})$  n.m.r. spectrum showed a broad resonance with  $^{195}\text{Pt}$  satellites at ambient temperature. Upon cooling the solution to  $-60^\circ\text{C}$  two species in approximately equal proportions were detected by  $^{31}\text{P}\text{-}({}^1\text{H})$  n.m.r. spectroscopy. One species was assigned the structure of the bis-alkoxo chelate complex (3.26). The other species showed an AB pattern but the  $^{195}\text{Pt}$  satellites were not resolved, [ $\delta\text{P}_\text{A}$  0.8 p.p.m.,  $\delta\text{P}_\text{B}$  3.0 p.p.m.,  $^2J(\text{P}_\text{A}\text{P}_\text{B}) = \sim 10.0\text{ Hz}$  (not fully resolved)]. This second species may be the binuclear compound (3.33) analogous to the known species (3.34).<sup>303</sup>

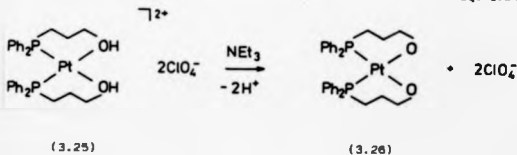




The complex  $[\text{PtBr}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  (3.27b) and the mixtures of cis- and trans-  $[\text{PtI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  (3.27c) and (3.28c) were cleanly deprotonated by NaOH in methanol to give in both cases the cis bis-alkoxo chelate complex (3.26) as shown by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy.

The bis-alkoxo chelate complex (3.26) was also obtained upon treatment of the dicationic complex (3.25) with  $\text{NEt}_3$  (eq. 3.14) as shown by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy.

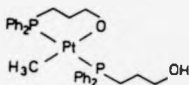
eq. 3.14



### 3.4.2 Reaction of $[\text{PtCl}(\text{CH}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$ with Sodium

#### Methoxide

The complex trans- $[\text{PtCl}(\text{CH}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})]$  (3.28b) on treatment with excess of NaOH in methanol gave a species whose  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectrum was an AB pattern with  $^{195}\text{Pt}$  satellites. The large  $^2J(\text{P}_\text{A}\text{P}_\text{B})$  coupling constant is consistent with the formation of the trans-alkoxo chelate complex (3.35),  $\delta^{31}\text{P}_\text{A}$  22.8 p.p.m.,  $^1J(\text{PtP}_\text{A}) = 3086 \text{ Hz}$ ,  $\delta\text{P}_\text{B}$  13.1 p.p.m.,  $^1J(\text{PtP}_\text{B}) = 3136 \text{ Hz}$ ,  $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 451 \text{ Hz}$ ].

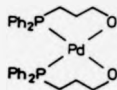


(3.35)

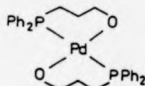
### 3.4.3 Reaction of $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$ with Sodium Methoxide

Upon treatment of  $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  in methanol with an excess of NaOH in methanol, the bright yellow precipitate dissolved to give a similar bright yellow solution. The  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectrum of the solution was a singlet resonance ( $\delta^{31}\text{P} = 22.2 \text{ p.p.m.}$ ). This species was not isolated, however, its structure may be possibly either the cis or trans bis-alkoxo chelate palladium(II) complex (3.36) or (3.37).





(3.36)



(3.37)

### 3.5 SOME REACTIONS OF THE BIS-ALKOXO CHELATE COMPLEX



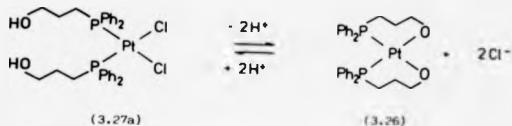
The following sections describe preliminary experiments to investigate the chemistry of the Pt-O bond in the chelates (3.26).

In each case the species are assigned on the basis of  $^{31}\text{P}$ - $(^1\text{H})$  n.m.r. spectroscopy only and therefore the assignments are tentative. However, similar species were obtained by Pringle *et al.*<sup>303</sup> which were more extensively characterized.

#### 3.5.1 Reaction of *cis*- $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$ with HCl

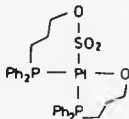
Treatment of the bis-alkoxo chelate complex (3.26) with dilute aqueous HCl gave the bis-phosphine complex (3.27a) quantitatively (as shown by  $^{31}\text{P}$ - $(^1\text{H})$  n.m.r. spectroscopy). Hence the conversion (3.27a) to (3.26) is reversible (eq. 3.15).

eq. 3.15



### 3.5.2 Reaction of cis-[Pt(Ph<sub>2</sub>POCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>] with SO<sub>2</sub>

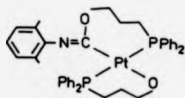
Sulphur dioxide was bubbled through a solution of the bis-alkoxo chelate complex (3.26) to determine whether the molecule would insert into the Pt-O bonds of the alkoxide. The <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum of the resulting solution showed an AB pattern. The <sup>195</sup>Pt satellites were not resolved but the small <sup>2</sup>J(P<sub>A</sub>P<sub>B</sub>) coupling constant is consistent with the phosphorus nuclei being mutually cis and the species is assigned structure (3.37) in which mono insertion of SO<sub>2</sub> has occurred, [<sup>31</sup>P<sub>A</sub> 13.3 p.p.m., <sup>δ</sup>P<sub>B</sub> 5.8 p.p.m., J(P<sub>A</sub>P<sub>B</sub>) = 17 Hz].



(3.37)

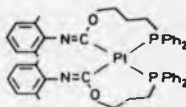
### 3.4.3 Reaction of cis-[Pt(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>] with 2,6-Dimethylphenylisocyanide

The reaction of the bis-alkoxo chelate complex (3.26) with one equivalent of 2,6-dimethylphenylisocyanide in methanol was rapid and led to the formation of the species (3.38) in solution. The <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum showed an AB pattern which was assigned to complex (3.38) in which the isocyanide had inserted into one of the Pt-O bonds of the alkoxide. The large <sup>2</sup>J(P<sub>A</sub>P<sub>B</sub>) coupling constant indicates that cis-trans isomerisation has occurred. [ $\delta$  P<sub>A</sub> 11.4 p.p.m., <sup>1</sup>J(PtP<sub>A</sub>) = 2554 Hz,  $\delta$  P<sub>B</sub> -0.5 p.p.m., <sup>1</sup>J(PtP<sub>B</sub>) = 2378 Hz, <sup>2</sup>J(P<sub>A</sub>P<sub>B</sub>) = 330 Hz].



(3.38)

Addition of two equivalents of 2,6-dimethylphenylisocyanide to the bis-alkoxo chelate complex (3.26) led to the formation of a single species in solution which showed a singlet resonance with 195Pt satellites in the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum. The product was assigned structure (3.39) in which the isocyanides have inserted into both of the Pt-O bonds. The observed <sup>1</sup>J(PtP) coupling constant is consistent with phosphorus trans to a ligand of high trans-influence. [ $\delta$  <sup>31</sup>P - 4.8 p.p.m., <sup>1</sup>J(PtP) = 1783 Hz].



(3.39)

### 3.5 DISCUSSION

The present work has shown that the functionalised phosphine  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH}$  (3.1) can be used to synthesise six membered chelate alkoxo platinum complexes which are similar to the five membered chelate complexes<sup>286,287</sup> in their stability towards air and water. It would appear that Pt-OR bonds are not inherently weak but that the observed instability of alkoxo compounds is due to kinetic effects i.e. facile  $\beta$ -hydrogen elimination.

In the chelate complexes containing the phosphine  $\text{Ph}_2\text{PCH}_2\text{CMe}_2\text{OH}$  (3.12) the absence of  $\beta$ -hydrogen atoms makes hydrogen elimination impossible. However, the chelate complexes containing  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OH}$  (3.13) or  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH}$  (3.2) appear to have similar stability and do contain  $\beta$ -hydrogens. It is the presence of the chelate rings which are the stabilising feature in these complexes. By analogy to metallocycloalkanes the  $\beta$ -hydrogens in the chelate rings are orientated away from the metal and thus the M-X-C-M (X = O or C) dihedral angle is far from the optimal  $0^\circ$  required for facile  $\beta$ -hydrogen elimination.<sup>20</sup>

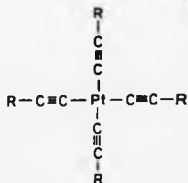
The suppression of the  $\beta$ -hydrogen elimination reaction by incorporation of the Pt-O bonds into chelating rings means that the chemistry and reactions involving Pt-O bonds can be more easily studied. Although the Pt-O bond is not weak, small molecules readily insert into the Pt-O bond forming new complexes.

## CHAPTER FOUR

SYNTHESIS AND CHARACTERISATION OF ACETYLIDE COMPLEXES OF  
PLATINUM(II) OF THE TYPE  $M'_2[Pt(C\equiv CR)_4]$ 

## 4.1 INTRODUCTION

Transition metal complexes containing acetylide ligands have been known for over thirty years but have not been extensively studied.<sup>305-320</sup> The complexes are often decomposed by water, acids and alkalis with formation of brown products.<sup>321</sup> The anionic acetylides are often particularly reactive because of the strongly basic character of the acetylide ligands and the anionic nature of the complex ions, causing these compounds to be extremely sensitive to protolysis.<sup>305</sup> In the present work a series of platinum(II) tetraacetylides  $[Pt(C\equiv CR)_4]^{2-}$  ( $R = Ph, Bu^t, CO_2Me, CO_2Et$ ) have been synthesised which have some stability towards air and moisture and have been characterised by  $^1H$ ,  $^{13}C$ - $\{^1H\}$  n.m.r. spectroscopy and infra-red spectroscopy.



- (4.1a)  $R = Ph$   
 (4.1b)  $R = Bu^t$   
 (4.1c)  $R = CO_2Me$   
 (4.1d)  $R = CO_2Et$

Acetylide ligands,  $RC\equiv C^-$ , are isoelectronic with cyanide ligands,  $N\equiv C^-$ , and stabilise anionic and/or low valent metal complexes. One explanation of this property is the delocalisation of electron density from the metal to the ligand i.e. contribution from canonical form B.

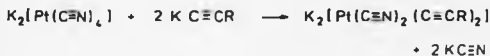


Acetylide and cyanide groups are similar in that they both possess low lying  $\pi^*$  orbitals of correct symmetry for  $d-\pi^*$  back bonding. If  $d-\pi^*$  back bonding did occur the M-C bonds would be expected to have considerable double bond character and consequently short M-C bond lengths. Although X-ray studies have found no evidence for M=C double bond character in neutral platinum(II) acetylides,<sup>310</sup> Molecular Orbital calculations and chemical studies are in favour of negative charge accumulation on the  $\beta$ -carbon of the acetylide.<sup>322</sup>

Cyanide and acetylide ligands are isoelectronic and are both linear ligands at the metal centre, therefore it may be expected that compounds containing the two ligands will have similar properties. Many acetylides are similar in formula, colour and magnetic properties to complex cyanides.<sup>305</sup>

Compounds which contain both cyanide and acetylide ligands in the coordination sphere of the metal have been prepared.<sup>308</sup> (e.g. eq. 4.1).

eq. 4.1



In view of the similarity between acetylide and cyanide ligands it was of interest to study the chemical and physical properties of  $[\text{Pt}(\text{C}\equiv\text{CR})_4]^{2-}$  in relation to  $[\text{Pt}(\text{CN})_4]^{2-}$  which is known to undergo partial oxidation to give one dimensional metal chain<sup>323</sup> complexes.

#### 4.1.1 TetracyanoPlatinum(II) Complexes

Several compounds containing the dianion  $[\text{Pt}(\text{CN})_4]^{2-}$  have been synthesised and studied by X-ray crystallography.<sup>324-329</sup> In every case the platinum(II) tetracyano complex crystallises into columnar stacks which contain linear or approximately linear, infinite chains of equally spaced platinum atoms (Fig. 4.1).<sup>330</sup> In the solid state such stacking leads to efficient packing.



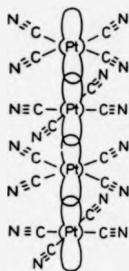


Fig. 4.1. Chain of square planar  $[\text{Pt}(\text{CN})_4]^{2-}$  groups showing the overlapping Pt  $d_z^2$  orbitals.<sup>330</sup>

The complexes associate through the vacant coordination site by Pt-Pt  $d_z^2$  overlap. The Pt-Pt separation  $d_{\text{Pt-Pt}}$  is strongly influenced by cation size, charge and degree of hydration. The intrachain separation  $d_{\text{Pt-Pt}}$  changes from a minimum of approximately 3.09 Å to 3.7 Å.

An example of this type of compound is  $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ <sup>329</sup> which consists of columnar stacks of  $[\text{Pt}(\text{CN})_4]^{2-}$  ions with  $d_{\text{Pt-Pt}}$  of 3.23 (3) Å. Adjacent groups are staggered with a torsion angle

of  $45^\circ$ . The Pt atom chains are bound together by a combination of  $\text{Ba}^{2+}$  ions and water molecule hydrogen bonded interactions.

The torsion angle between adjacent  $[\text{Pt}(\text{CN})_4]^{2-}$  ions have been found to vary from  $45^\circ$  corresponding to a staggered configuration to a totally eclipsed configuration of  $0^\circ$ . Generally compounds with short  $d_{\text{Pt-Pt}}$  have a torsion angle of  $45^\circ$  which should minimize CN group repulsion interactions while those with a long  $d_{\text{Pt-Pt}}$  have eclipsed configurations.<sup>330</sup>

In very concentrated aqueous solution, self association of  $[\text{Pt}(\text{CN})_4]^{2-}$  occurs to give oligomeric species  $[\text{Pt}(\text{CN})_4]_3^{6-}$  which can be detected by absorption and emission.<sup>331</sup>

#### 4.1.2 Partially Oxidised Tetracyanoplatinate Complexes

Divalent tetracyanoplatinum complexes upon partial oxidation give rise to a novel type of compound generally known as partially oxidised tetracyanoplatinate (POTCP) complexes.<sup>330</sup> These complexes contain Pt atoms which are in a non integral oxidation state and also contain columnar stacks of square planar tetracyanoplatinate groups but with a decreased intrachain separation  $d_{\text{Pt-Pt}}$  of  $3.0 \text{ \AA}$  or less.

The interesting feature of these compounds is their highly anisotropic physical properties. POTCP complexes generally have brilliant metallic lustrous and are excellent one dimensional metallic conductors. Measurements of the electrical conductivity parallel to the Pt chain are of the order of  $10^5$  greater than the conductivity perpendicular to the chain direction.<sup>330</sup>

Many of the properties of POTCP can be explained in terms of conduction electrons in a delocalized energy band formed by the overlap of  $5d_{x^2}$  orbitals. In  $K_2[Pt(CN)_4]$  the atoms in the chain <sup>323,331-333</sup> on close approach of the platinum  $5d_{x^2}$  band is fully occupied but under partial oxidation a fraction of the electrons are removed from the highest level of the  $d_{x^2}$  band reducing the average energy of the electrons in the band and forming a partially filled conduction band (see Fig. 4.2).

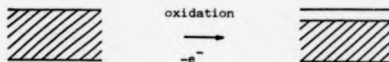


Fig. 4.2. The number of electrons removed from the energy band is determined by the degree of partial oxidation.

As electrons are removed from the band the bonding in the chain is strengthened resulting in a decrease in the Pt-Pt intrachain separations. Addition of negatively charged particles or removal of positively charged particles is necessary to preserve the electrical neutrality of the lattice. This explains the formation of cation deficient salts such as  $M_{1.75}[Pt(CN)_4] \cdot xH_2O$ ,  $M = Li, K, Rb, Cs$ <sup>334,335</sup> and the more common anion-deficient

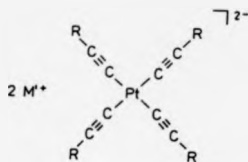
complexes such as  $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ .<sup>336</sup>

Thus it is the presence of a partially occupied  $d_x$  bond which leads to metallic conduction.

POTCP complexes containing a partially filled band require partial oxidation of a  $Pt^{2+}$  salt to form a non integral oxidation state in their synthesis. There are three methods in which this may be achieved; (i) mixing solutions of the appropriate  $Pt^{2+}$  and  $Pt^{4+}$  salt. For example, evaporation of an aqueous solution containing the complex salts  $K_2[Pt(CN)_4]$  and  $K_2[Pt(CN)_4Cl_2]$  in a molar ratio of 5:1 gives needles with a coppery sheen having the composition  $K_2[Pt(CN)_4]Cl_{0.32} \cdot 2.6 H_2O$ .<sup>337</sup>; (ii) by chemical oxidation of the  $Pt^{2+}$  salt;<sup>338</sup> (iii) by electrolysis using a dc voltage source and a potential of 0.75 - 1.5 V.<sup>339-341</sup>

#### 4.2 AIMS AND SCOPE OF PRESENT WORK

The four platinum(II) tetracyanide complexes  $M'_2[Pt(C\equiv CR)_4]$  (4.1a-d) were synthesised and characterised and the effect of the electronegativity of the R group on the stability of the complexes was investigated.



(4.1a)  $\text{M}^+ = \text{K}^+$ ,  $\text{R} = \text{Ph}$

(4.1b)  $\text{M}^+ = \text{K}^+$ ,  $\text{R} = \text{Bu}^t$

(4.1c)  $\text{M}^+ = [\text{N}(\text{PPh}_3)_2]^+$ ,  $\text{R} = \text{CO}_2\text{Me}$

(4.1d)  $\text{M}^+ = [\text{N}(\text{PPh}_3)_2]^+$ ,  $\text{R} = \text{CO}_2\text{Et}$

No crystal structures of anionic acetylide complexes of the type above have been determined. The crystal structure of  $\text{K}_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$  (4.1a) was obtained to determine whether columnar stacks of Pt atoms would occur in the solid state as in  $\text{K}_2[\text{Pt}(\text{CN})_4]$ . If columnar stacking did occur, it would be of interest to determine whether the corresponding partially oxidised tetraacetylide platinum complex could be synthesised.

The crystal structure of  $\text{K}_2[\text{Pt}(\text{C}\equiv\text{CBu}^t)_4]$  (4.1b) was also obtained to determine whether the presence of bulky groups would disrupt columnar stacking of the platinum(II) atoms since the bulkiness of the groups may lead to a Pt-Pt separation where effective overlap of the  $5d_z^2$  orbitals cannot occur.

The chemistry of the compounds  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) and  $K_2[Pt(C\equiv CBu^t)_4]$  (4.1b) in solution was investigated by electrochemical methods to determine whether a partially oxidised tetraacetylide platinum complex may be prepared.

#### 4.3 SYNTHESIS OF COMPOUNDS OF THE TYPE $M'_2[Pt(C\equiv CR)_4]$

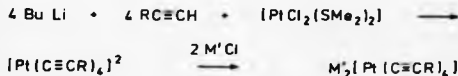
Metal acetylides of the type  $M'_2[M(C\equiv CR)_4]$  (where  $M' = Li^+$ ,  $K^+$ ,  $M = Ni^{2+}$ ,  $Pd^{2+}$ ,  $Pt^{2+}$ ) are usually prepared by treating the thiocyanate or nitrate of the metal  $M$  with the alkali metal  $M'$  acetylide in liquid ammonia (e.g. eq. 4.2).<sup>308</sup>

eq. 4.2



In the present work the platinum(II) tetraacetylides (4.1a-d) were synthesised by the method shown in eq. 4.3.

eq.4.3



The compounds were isolated as solids which were stable to air and moisture for short periods. To avoid decomposition the compounds were stored in vacuo over  $P_2O_5$ . The compounds  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) and  $K_2[Pt(C\equiv CBu^t)_4]$  (4.1b) were soluble in water or chloroform. Aqueous solutions of (4.1a) and (4.1b), if left for several hours darkened and turned into thick colloidal gels. To avoid decomposition, the two compounds were recrystallised from water in the presence of KOH. Crystals of hydrated  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) were stable in air but those of hydrated  $K_2[Pt(C\equiv CBu^t)_4]$  (4.1b) immediately lost solvent on exposure to air and were therefore handled in a water-saturated atmosphere.

#### 4.4 SPECTRAL CHARACTERISATION OF COMPOUNDS OF THE TYPE



The  $^1H$  n.m.r. spectra of compounds (4.1a-d) (data given in Table 4.1) show the presence of the expected resonances attributed to the R group and in the spectra of compounds (4.1c) and (4.1d) the presence of additional resonances due to the cation  $[N(PPh_3)_2]^+$  are observed. The resonances are sharp indicating that no exchange of coordinated and free acetylene was occurring in solution.

The  $^{13}C$ - $^1H$  n.m.r. spectra (data given in Table 4.2) of compounds (4.1a-d) show a singlet resonance with  $^{195}Pt$  satellites for the  $\alpha$ -carbon of the acetylide ligand.

The infra-red spectra of the compounds (4.1a-d) (data given in Table 4.3) show the presence of a band in the region 2050-2100  $cm^{-1}$  due to the stretching of the carbon carbon triple bonds of the acetylide ligands. Compounds (4.1a) and (4.1b) both contain

Table 4.1.  $^1\text{H}$  n.m.r. data<sup>a</sup> for compounds of the type  $\text{M}'_2 [\text{Pt}(\text{CNR})_4]$ 

Compound	$\delta$ R Group Resonances	Multiplicity	$\delta$ Cation $\text{M}'$ Resonance (multiplicity)
(4.1a) <sup>b</sup> R = Ph $\text{M}' = \text{K}^+$	7.08-7.68	s	-
(4.1b) <sup>b</sup> R = Bu <sup>t</sup> $\text{M}' = \text{K}^+$	1.18	s	-
(4.1c) <sup>c</sup> R = $\text{CO}_2\text{Me}$ $\text{M}' = [\text{N}(\text{Ph})_3]_2^+$	3.58	s	7.50 - 7.88 (m)
(4.1d) <sup>c</sup> R = $\text{CO}_2\text{Et}$ $\text{M}' = [\text{N}(\text{Ph})_3]_2^+$	1.12	t, (J = 8 Hz)	7.48 - 7.86 (m)
$\text{M}' = [\text{N}(\text{Ph})_3]_2^+$	4.07	q, (J = 8 Hz)	

<sup>a</sup> Spectra (220 MHz) measured at ambient temperature. Chemical shifts ( $\delta$ ) in p.p.m.( $\pm 0.01$ ) to high frequency of  $\text{SiMe}_4$  and coupling constants J in Hz ( $\pm 0.1$ ).

Multiplicities: s = singlet, m = multiplet, t = triplet, q = quartet.

<sup>b</sup> Recorded in  $\text{D}_2\text{O}$ .<sup>c</sup> Recorded in  $\text{CDCl}_3$ .



Table 4.2.  $^{13}\text{C}$ -[H] N.m.r. data<sup>a</sup> for compounds of type  $\text{M}'_2[\text{Pt}(\text{C}^1=\text{C}^2)_2]$ .

Compound	$\delta(\text{C}^1)$	$\delta(\text{C}^2)$	$\delta(\text{Other Resonances in R group})$	$\delta(\text{Cation M}' Resonances (multiplicity))$
(4.1a) <sup>b</sup> R = Ph M' = K <sup>+</sup>	103.6 (t, $^1\text{J}(\text{CPT})=316$ Hz)	117.2 (s)	123.4 (s), 127.8 (s), 131.2 (s).	-
(4.1b) <sup>b</sup> R = Bu <sup>t</sup> M' = K <sup>+</sup>	116.7 (t, $^1\text{J}(\text{CPT})=280$ Hz)	95.2 (s)	29.6 (s), 32.6 (s).	-
(4.1c) <sup>c</sup> R = CO <sub>2</sub> Me M' = [K(Ph <sub>3</sub> P) <sub>2</sub> ] <sup>+</sup>	96.1 (t, $^1\text{J}(\text{CPT})=299$ Hz)	124.3 (s)	52.3 (s), 150.0 (s), 132.4 (s), 134.2 (s).	127.2 (d, $^1\text{J}(\text{CP})=107.8$ Hz), 120.9 (s), 132.4 (s), 134.2 (s).
(4.1d) <sup>c</sup> R = CO <sub>2</sub> Et M' = [K(Ph <sub>3</sub> P) <sub>2</sub> ] <sup>+</sup>	96.4 (t, not resolved)	124.4 (s)	14.9 (s), 61.1 (s), 155.8 (s), 132.4 (s), 134.2 (s).	127.2 (d, $^1\text{J}(\text{CP})=107.7$ Hz), 129.9 (s).

<sup>a</sup> Spectra measured at 100.6 Hz in D<sub>2</sub>O at ambient temperature. Multiplicities: s = singlet, d = doublet, t = virtual triplet.

<sup>b</sup> Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm 0.1$ ) to high frequency of SiMe<sub>4</sub> and coupling constants  $J$  in Hz ( $\pm 0.1$ ).

<sup>c</sup> Recorded in CDCl<sub>3</sub>.

Table 4.3. Infrared data<sup>a</sup> for compounds of the type  $M'_2[Pt(CtCR)_4]$ .

Compound	$\nu(CtC)/cm^{-1}$	Other bands/ $cm^{-1}$
(4.1a) R = Ph $M' = K^+$	2090s	$\nu(OH)$ 3400br, $\nu(C-C)$ 1595s, $\nu(Ph-H)$ 695s, 710s
(4.1b) R = Bu <sup>t</sup> $M' = K^+$	2090s	$\nu(O-H)$ 3400br, $\nu(C(CH_3)_3)$ 1380m, 1365m
(4.1c) R = $CO_2Me$ $M' = [N(CPh_3)_2]^+$	2085s	$\nu(C-O)$ 1675s, $\nu(C-O)$ 1115m, $\nu(P-Ph)$ 1460s, $\nu(N-P)$ 1240s, $\nu(Ph-H)$ 725s, 690s.
(4.1d) R = $CO_2Et$ $M' = [N(CPh_3)_2]^+$	2085s	$\nu(C-O)$ 1660s, $\nu(C-O)$ 1065s, $\nu(P-Ph)$ 1460s, $\nu(N-P)$ 1210s, $\nu(Ph-H)$ 720s, 695s.

<sup>a</sup> Cesium iodide disc.

bands due to the stretching of an O-H bond indicating that water is present in the structure. Bands can also be assigned to the stretching of bonds in the functional groups in the R group of the acetylide ligand and in the case of compounds (4.1c) and (4.1d), in the cation ligand.

#### 4.5 SOLUTION CHEMISTRY OF $K_2[Pt(C\equiv CPh)_4]$ AND $K_2[Pt(C\equiv CBU^t)_4]$

Preliminary experiments were carried out to investigate the electrochemistry of  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) and  $K_2[Pt(C\equiv CBU^t)_4]$  (4.1b) in solution using cyclic voltammetry.

Fig. 4.3 shows a typical cyclic voltammogram at a Pt electrode for  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) (0.2 mmol) and triethylamino-tetrafluoroborate (TEATFB) (0.1 M) in acetonitrile. In all cases a single oxidation wave was observed [ $E_{p,a} = 0.64$  V vs saturated calomel electrode (S.C.E.)], with no corresponding reduction wave. Plots of  $i_{p,a}$  against  $\sqrt{v}$  were linear indicating that the species freely diffusing in solution were being oxidised. Presumably the product of the oxidation of the  $[Pt(C\equiv CPh)_4]^{2-}$  is unstable in this solution and is lost by rapid follow up reaction.

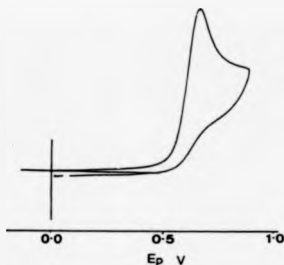


Fig. 4.3. Cyclic Voltammogram of  $K_2[Pt(C_6CPh)_4]$  in acetonitrile,  $0.1 \text{ mol dm}^{-3}$  TEATFB. Scan rate  $100 \text{ mV s}^{-1}$ , vs S.C.E. using a platinum working electrode.

The electrochemistry of  $K_2[Pt(C_6CPh)_4]$  ( $0.2 \text{ mmol}$ ) was also investigated in aqueous solution containing  $0.1 \text{ M KCl}$ . In this case (Fig. 4.4), an insulating 'gold' film forms on the first anodic cycle which blocks further oxidation of the platinum complex. Integration of the total charge possessed in forming the film indicates that of the order of  $10^{-10} \text{ mol cm}^{-2}$  of material are involved (assuming  $n = 1$ ). Attempts to overcome this problem by the use of  $0.1 \text{ M KCN}$  as the background electrolyte were unsuccessful as it gave essentially identical results.

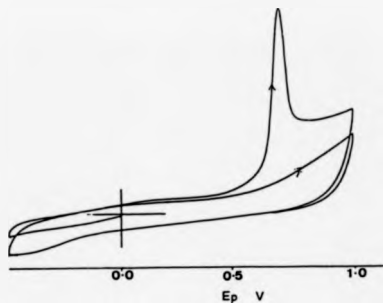


Fig. 4.4. Cyclic voltammogram of  $K_2[Pt(C_6CPh)_4]$  in water,  $0.1 \text{ mol dm}^{-3}$  KCl. Scan rate  $100 \text{ mV s}^{-1}$ , vs S.C.E. Formation of an insulating gold film (2) prevents further oxidation.

Cyclic voltammetry of  $K_2[Pt(C_6CtBu)_4]$  (4.1b) ( $0.2 \text{ mmol}$ ) in aqueous  $0.1 \text{ M}$  KCl (Fig. 4.5) shows a single anodic peak at  $1.11 \text{ V}$  vs S.C.E. with no evidence for any reverse peak, again indicating that the oxidised compound is unstable under these conditions. Plots of  $i_{pa}$  against  $\sqrt{v}$  were again linear as expected for a solution redox couple.

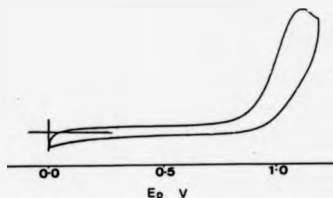


Fig. 4.5. Cyclic voltammogram of  $K_2[Pt(C\equiv CBu^t)_4]$  in water, 0.1 mol dm<sup>-3</sup> KCl. Scan rate 100 mV s<sup>-1</sup>, vs S.C.E.

A problem encountered in the above experiments was the instability in solution of the  $Pt^{2+}$  species and the oxidised  $Pt^{4+}$  species. As the electrochemistry was being carried out, the solutions of (4.1a) and (4.1b) in aqueous 0.1 M KCl turned brown over a period of 15 min. However the experiments clearly show that both  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) and  $K_2[Pt(C\equiv CBu^t)_4]$  (4.1b) can be oxidised in solution. It may therefore be possible to produce partially oxidised complexes of  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) and  $K_2[Pt(C\equiv CBu^t)_4]$  (4.1b) if the correct medium can be found.

Partially oxidised tetracyanoplatinum complexes can be synthesised by mixing solutions of the appropriate  $Pt^{2+}$  and  $Pt^{4+}$  salts. An understanding of the solution behaviour of  $[Pt(CN)_4]^{2-}$ ,  $[Pt(CN)_4X_2]^{2-}$  and  $K_2[Pt(CN)_4] \cdot x_{0.3}$  may shed light on the chain formation and crystallisation mechanisms.

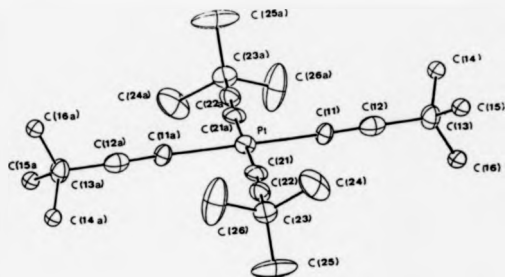


Fig. 4.6. View of molecule of  $[\text{Pt}(\text{C}_8\text{CBu}^t)_4]^{2-}$  showing the atomic numbering.

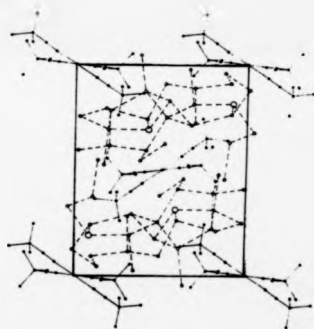


Fig. 4.7. View of molecules of  $\text{K}_2[\text{Pt}(\text{C}_8\text{CBu}^t)_4]$  in unit cell showing water of crystallisation.

Table 4.4. Selected bond distances (Å) and bond angles (°) for



## Bond distances (Å)

Pt-C(11)	2.014 (10)
Pt-C(21)	2.021 (13)
C(11)-C(12)	1.221 (14)
C(12)-C(13)	1.499 (15)
C(13)-C(14)	1.511 (22)
C(13)-C(15)	1.565 (19)
C(13)-C(16)	1.543 (20)
C(21)-C(22)	1.204 (19)
C(22)-C(23)	1.513 (20)
C(23)-C(24)	1.554 (49)
C(23)-C(25)	1.547 (50)
C(23)-C(26)	1.527 (59)
K(1)-O(6)	2.832 (12)
K(1)-O(7)	2.891 (10)
K(1)-O(11)	2.868 (11)

## Bond angles (°)

C(11)-Pt-C(21)	90.9 (5)
C(21)-Pt-C(11a)	89.1 (5)
C(11)-Pt-C(11a)	180.0
Pt-C(11)-C(12)	176.8 (11)
C(11)-C(12)-C(13)	177.2 (13)
C(12)-C(13)-C(14)	110.0 (10)
C(12)-C(13)-C(15)	107.5 (10)
C(12)-C(13)-C(16)	106.2 (10)
C(14)-C(13)-C(15)	109.8 (13)
C(14)-C(13)-C(16)	111.5 (12)
C(15)-C(13)-C(16)	109.6 (11)
Pt-C(21)-C(22)	177.8 (10)
C(21)-C(22)-C(23)	176.4 (13)
C(22)-C(23)-C(24)	109.5 (24)
C(22)-C(23)-C(25)	108.3 (23)
C(22)-C(23)-C(26)	115.6 (23)



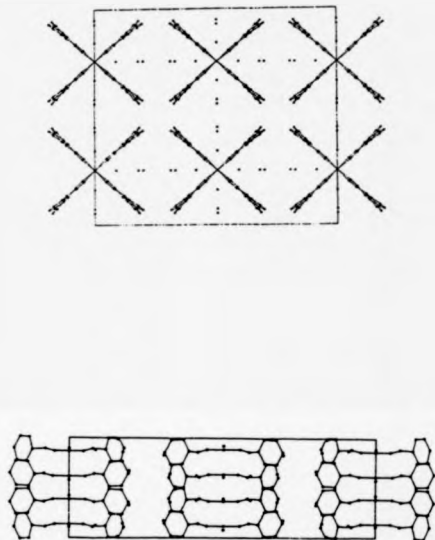


Fig. 4.8. Two views a) and b) showing the stacking of the  $[\text{Pt}(\text{C}_8\text{CPh})_4]^{2-}$  groups into chains in the unit cell.

#### 4.6 X-RAY CRYSTAL STRUCTURE OF $K_2[Pt(CsCBu^t)_4]$

Selected bond lengths and angles (with numbering scheme shown in Fig. 4.6) are listed in Table 4.4.

The crystal structure of one half of the molecule was determined and the other half generated by symmetry.

In the  $[Pt(CsCBu^t)_4]^{2-}$  dianion the square planar geometry around the platinum atom is slightly distorted, subject to the  $\bar{1}$  symmetry.

Both the independent Pt-Cs-C linkages deviate slightly from linearity. The Pt-C(11)-C(12) bond angle is  $176.8 (11)^\circ$  and the C(11)-C(12)-C(13) bond angle is  $177.2 (13)^\circ$ . The Pt-C(21)-C(22) bond angle is  $17.78 (10)^\circ$  and C(21)-C(22)-C(23) bond angle is  $176.4 (13)^\circ$ .

The large thermal parameters of the methyl groups of the tert-butyl groups probably rise from a combination of dynamic movement and static disorder. Two positions were observed for each methyl carbon atom of one tert-butyl group, while the other was rather better ordered.

A very surprising feature of the crystal structure was the number of water molecules present in the crystal (Fig. 4.7). The number of 28 water molecules per  $K_2[Pt(CsCBu^t)_4]$  unit is a very high degree of hydration.

It can be seen from Fig. 4.7 that stacking of the  $[Pt(CsCBu^t)_4]^{2-}$  groups into infinite chains does not occur. It is presumed that the bulky tert-butyl groups prevent this from occurring. The resulting separation between two Pt atoms is  $11.98 \text{ \AA}$ .

#### 4.7. X-RAY CRYSTAL STRUCTURE OF $K_2[Pt(C\equiv CPh)_4]$

The crystal structure determination of  $K_2[Pt(C\equiv CPh)_4]$  is being solved by Dr. N. Alcock and requires further refinement and therefore selected bond lengths and angles are not included in the present work. However the general information obtained about the crystal structure of  $K_2[Pt(C\equiv CPh)_4]$  is discussed here in order to compare with  $K_2[Pt(C\equiv C^tBu)_4]$ .

In the  $[Pt(C\equiv CPh)_4]$  dianion the square planar geometry around the platinum atom is slightly distorted. An interesting feature is that stacking of the  $[Pt(C\equiv CPh)_4]$  groups into infinite chains does occur (Fig. 4.8) with eclipsing of the acetylide groups. The intrachain separation between two Pt atoms is 4.80 and 5.05 Å (alternate). The  $K^+$  cations and water molecules occupy the space between the chains.

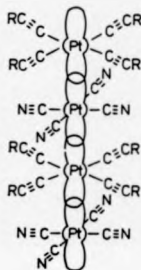
#### 4.8 DISCUSSION

The X-ray crystal structure of  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) and the preliminary electrochemistry experiments indicate that oxidation of  $K_2[Pt(C\equiv CPh)_4]$  (4.1a) is possible and the  $[Pt(C\equiv CPh)_4]^{2-}$  groups do stack in chains. It may therefore, be possible to obtain partially oxidised tetraacetylide complexes by one of the methods outlined in Section 4.1.2. The bulky tert-butyl groups of the acetylide ligand in  $K_2[Pt(C\equiv C^tBu)_4]$  (4.1b) would appear to prevent partial oxidation occurring with concurrent chain formation.

It may be possible to systematically change the acetylide ligand  $^-(C\equiv CR)$  by varying R to tune the properties of  $M'_2[Pt(C\equiv CR)_4]$  so that one-dimensional systems can be obtained with perhaps

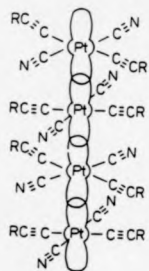
differing properties.

By mixing solutions of the divalent tetraacetylide platinum complexes with the tetravalent tetracyanoplatinum complex or vice-versa, a partially oxidised platinum complex containing both  $[\text{Pt}(\text{CN})_4]^{2-}$  and  $[\text{Pt}(\text{C}\equiv\text{CR})_4]^{2-}$  groups may be synthesised (e.g. 4.2).



(4.2)

Finally, partially oxidised platinum complexes in which the groups in the chain contain both acetylide and cyano ligands in the same coordination sphere (eg. 4.3) of the platinum may be possible.



(4, 3)

## EXPERIMENTAL

## GENERAL CHEMICAL PROCEDURES

In general, reactions were carried out under an inert atmosphere of argon or nitrogen using standard techniques for handling air-sensitive compounds. Solvents were purified by distillation from sodium-benzophenone (tetrahydrofuran, diethylether) or calcium hydride (benzene, dichloromethane, methanol). Chemicals used in the course of the present work were either obtained commercially and used without further purification unless otherwise stated, or synthesised by literature methods. Rare metal compounds were obtained from Johnson Matthey PLC.

$^1\text{H}$  n.m.r. spectra were recorded at either 220 MHz using a Perkin-Elmer R34 spectrometer, 90 MHz using a Bruker WH90 Spectrometer or 400 MHz using a Bruker WH400 spectrometer. Chemical shifts (in  $\text{CDCl}_3$ ,  $\text{D}_2\text{O}$ , methanol- $\text{d}_4$  or benzene- $\text{d}_6$ ) are to high frequency of tetramethylsilane (internal standard).  $^1\text{H}$ - $\{^{31}\text{P}\}$  n.m.r. spectra were recorded at 400 MHz on a Bruker WH400 spectrometer at Edinburgh University by Dr. Sadler.

$^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectra were recorded at either 36.4 MHz using a Bruker WH90 spectrometer or at 162.0 MHz using a Bruker WH400 spectrometer.  $^{31}\text{P}$  n.m.r. shifts (in  $\text{CDCl}_3$ , methanol- $\text{d}_4$  or benzene- $\text{d}_6$ ) are to high frequency of 85%  $\text{H}_3\text{PO}_4$  (external standard).

$^{195}\text{Pt}$ - $\{^1\text{H}\}$  n.m.r. spectra were recorded at 85.6 MHz using a Bruker WH400 spectrometer.

$^{13}\text{C}$ -( $^1\text{H}$ ) n.m.r. spectra were recorded at 100.6 MHz on a Bruker WH400 spectrometer. Chemical shifts (in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$ ) are to high frequency of tetramethylsilane.

Infra-red spectra were recorded on a Perkin-Elmer 580B spectrometer ( $4000\text{--}200\text{ cm}^{-1}$ ) as Nujol mulls on cesium iodide plates or as potassium bromide discs.

Mass spectra were recorded using a Kratos MS80 instrument.

Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex, U.K.

## E.2.1 PREPARATION OF PLATINACYCLOHEXANES AND 9,10-DIHYDRO-9-PLATINAANTHRACENES

**Preparation of 1,5-Dilithiopentane.** - This was made according to the method of Whitesides et al.<sup>20</sup> in 83% yield (Lit. 85%). The concentration of the lithium reagent was determined by a modification of Gilman's double titration method.<sup>275</sup>

**Preparation I of  $[(PPh_3)_2Pt(CH_2)_5]$ .** - 1,5-Dilithiopentane (2.2 cm<sup>3</sup>, 0.89 M in diethylether, 1.96 mmol) was added dropwise over 15 min to a stirred suspension of  $[PtCl_2(SMe_2)_2]$  (0.50 g, 1.28 mmol) in diethylether (40 cm<sup>3</sup>) cooled to -45 °C. The reaction mixture was then stirred for 1 h and allowed to warm to 0 °C. A solution of  $PPh_3$  (0.67 g, 2.56 mmol) in diethylether (5 cm<sup>3</sup>) was added to the mixture after cooling it to -45 °C. The reaction mixture was then stirred for 24 h and allowed to warm up to ambient temperature. Methanol (10 cm<sup>3</sup>) was added to the yellow mixture and the volume reduced to 10 cm<sup>3</sup> by evaporation under reduced pressure. The off white solid product was then filtered off and washed with methanol (20 cm<sup>3</sup>) and diethylether (30 cm<sup>3</sup>). The product was recrystallised by dissolving in dichloromethane (15 cm<sup>3</sup>) and adding ethanol (10 cm<sup>3</sup>). The solution was heated on a steam bath until the appearance of crystals. The solution was then cooled slowly to 0 °C and then to -20 °C. The white crystalline product was filtered off, washed with ethanol (10 cm<sup>3</sup>) and diethylether (20 cm<sup>3</sup>) and dried in vacuo over  $P_2O_5$ . Yield 0.74 g, 73%.

<sup>13</sup>C-(<sup>1</sup>H) n.m.r. data for phosphine ligand resonances given in Table E.2.1.1.



Preparation of 1,5-bis(bromomagnesium)pentane

This was prepared from 1,5-dibromopentane according to the method of Whitesides *et al.*<sup>20</sup> in 90% yield.

Preparation II of  $[(PPh_3)_2Pt(CH_2)_5]$ . - 1,5-Bis(bromomagnesium)pentane (4.0 cm<sup>3</sup>, 0.45 M in a mixture of diethylether and tetrahydrofuran, 1.8 mmol) was added dropwise over 15 min to a stirred suspension of  $[PtCl_2(1,5-COD)]$  (0.374 g, 1.0 mmol) in diethylether (50 cm<sup>3</sup>) and tetrahydrofuran (30 cm<sup>3</sup>) cooled to -50 °C. The mixture was stirred for 1 h and allowed to warm to 0 °C. A solution of  $PPh_3$  (0.524 g, 2.0 mmol) in diethylether (5 cm<sup>3</sup>) was then added to the clear solution after again cooling it to -50 °C. The mixture was then stirred for 16 h and allowed to warm to ambient temperature. Ethanol (10 cm<sup>3</sup>) was added and the volume reduced to 10 cm<sup>3</sup> by evaporation under reduced pressure. The off-white solid product was filtered off. Recrystallisation from dichloromethane/ ethanol 3:2 v/v gave a white crystalline solid. Yield 0.61 g, 75%.

Preparation of  $[(PhH)_2P]_2Pt(CH_2)_5]$ . - This was made according to the method of Whitesides *et al.*<sup>20</sup> in 10% yield. Recrystallisation from dichloromethane/methanol 1:2 v/v gave yellow brown irregular plate crystals suitable for X-ray crystal structure determination.

<sup>13</sup>C-<sup>1</sup>H n.m.r. data for phosphine ligand resonances are given in Table E.2.1.1.

**Preparation of 1,5-Dibromo-3-methylpentane.** - This was prepared using an adaptation of the method of Johnson et al., 267

Conc. sulphuric acid (200 g) was added with care to a stirred solution of 3-methyl-1,5-pentanediol (118.0 g, 1.0 mol) and 48% hydrobromic acid (600 g, 3.5 mol). The mixture was then heated under reflux for 3 h. The mixture was left to cool and then the two resulting layers separated. The aqueous layer was extracted with dichloromethane (3 x 200 cm<sup>3</sup>). The combined organic layer and washings were dried over calcium chloride and filtered. The solvent was removed under reduced pressure. Distillation under reduced pressure gave the colourless liquid product. Yield 162.2 g, 68% [b.p. 106°C, 12 mm Hg;

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 220 MHz): δ 0.92 (3H, d, J=6 Hz), 1.5-2.0 (5H, m), 3.44 (4H, m) p.p.m.]

**Preparation of 1,5-Dilithio-3-methylpentane.** - This was prepared at -45 °C using a similar procedure to 1,5-dilithiopentane in 60% yield.

**Preparation of 1,5-bis(bromomagnesium)-3-methylpentane.** - This was prepared using a similar procedure to 1,5-bis(bromomagnesium) pentane in 83% yield.

**Preparation of  $[(PPh_3)_2Pt(CH_2CH_2CH(CH_3)CH_2CH_2)]_n$ .** - This was prepared using similar procedures (I and II) to  $[(PPh_3)_2Pt(CH_2CH_2)]_n$ . Both methods gave a white air stable which was recrystallised from dichloromethane/ethanol 3:2 v/v. Procedure I using 1,5-dilithio

-3-methylpentane gave a slightly higher yield. Yield using procedure I 0.75 g, 73% and using procedure II 0.63 g, 65%.

$^{13}\text{C}$ - $^1\text{H}$  n.m.r. data for phosphine ligand resonances given in Table E.2.1.1.

**Preparation of Diethyl- $\beta,\beta$ -dimethylglutarate.** - This was made using an adaptation of Micovic's method<sup>268</sup> to esterify adipic acid.

A mixture of  $\beta,\beta$ -dimethylglutaric acid (100 g, 0.625 mol), ethanol (225 cm<sup>3</sup>, 1.875 mol) toluene (112.5 cm<sup>3</sup>) and conc. sulphuric acid (0.5 cm<sup>3</sup>) were placed in a 1000 cm<sup>3</sup> flask. The mixture was then heated to a temperature of 78 °C at which the azeotropic mixture of ethanol, toluene and water distilled. The distillate was collected over anhydrous  $\text{K}_2\text{SO}_4$  (94 g) and filtered. The distillate was then returned to the flask and the azeotropic mixture again distilled at 78 °C. The residue was left to cool and then distilled under reduced pressure to give the colourless liquid product. Yield 118 g, 88%.

[b.p. 64 °C, 0.3 mm Hg;

$^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 220 MHz):  $\delta$  1.14 (6H, s), 1.26 (6H, t, J=7 Hz), 2.42 (4H, s), 4.12 (4H, t, J=7 Hz) p.p.m. ]

**Preparation of 3,3-Dimethyl-1,5-pentanediol.** - This was made using the method of Wheeler *et al.*<sup>269</sup> Diethyl- $\beta,\beta$ -dimethylglutarate (81.6 g, 0.37 mol) in diethylether (80 cm<sup>3</sup>) was added dropwise to a vigorously stirred suspension of lithium aluminium hydride (20.0 g, 0.53 mol) in diethylether (750 cm<sup>3</sup>). Complete addition required 2 h. The mixture was then stirred for a further 2 h. Water (20 cm<sup>3</sup>),

15% sodium hydroxide (20 cm<sup>3</sup>) and water (60 cm<sup>3</sup>) were then added successively, and the inorganic solid filtered off and washed with diethylether (2 x 100 cm<sup>3</sup>). The combined washings and filtrate were evaporated to dryness under reduced pressure to yield the colourless liquid product. Yield 43.5 g, 88%.

[<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 220 MHz); 60.94 (6H, s), 1.56 (4H, t, J=8 Hz), 3.48 (2H, br s), 3.69 (4H, t, J=8 Hz) p.p.m.].

Preparation of 1,5-Dibromo-3,3-dimethylpentane. - This was prepared using a similar procedure to 1,5-dibromo-3-methylpentane.

Distillation under reduced pressure gave a colourless liquid. Yield 53 g, 83%.

[b.p. 60 °C, 0.6 mm Hg;

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 400 MHz); 6 0.96 (6H, s), 1.84 (4H, AA'MM' spin system, [J(AM) + J(AM')] = 17.2 Hz), 3.35 (4H, AA'MM' spin system, [J(AM) + J(AM')] + 17.2 Hz) p.p.m.].

Preparation of 1,5-Dithio-3,3-dimethylpentane. - This was prepared at -40°C using a similar procedure to 1,5-dithiopentane in 41% yield.

Preparation of 1,5-bis(bromomagnesium)-3,3-dimethylpentane. - This was prepared using a similar procedure to 1,5-bis(bromomagnesium) pentane in 75% yield.

Preparation of  $[(PPh_3)_2Pt(CH_2CH_2C(CH_3)_2CH_2CH_2)]$  - This was prepared using similar procedures (I and II) to  $[(PPh_3)_2Pt(CH_2)_5]$ . Both methods gave a white air stable solid which was recrystallised from dichloromethane/ethanol 3:2 v/v. Procedure II using 1,5-bis(bromo-magnesium)-3,3-dimethylpentane gave a higher yield. The yield using procedure I 0.25 g, 49% and using procedure II 0.58 g, 71%.

$^{13}C$ - $^1H$  n.m.r. data for phosphine ligand resonances given in Table E.2.1.1. .

Preparation of  $[(PPh_3)_2Pt(CH_2CH_2C(CH_3)_2CH_2CH_2)]$  - This was prepared in a similar manner to  $[(PPh_3)_2Pt(CH_2)_5]$  using procedure II in 10% yield. Recrystallisation from dichloromethane/methanol 1:2 v/v gave yellow crystals suitable for X-ray structure determination.

Preparation of Dimethylglutarate-2,2,4,4- $d_4$  - This was prepared according to the method of Lambert *et al.*<sup>231</sup> A mixture of dimethylglutarate (36.8 g, 0.23 mol), methanol- $d_4$  (36.2 g, 1.09 mol) and 5% sodium methoxide was allowed to stir for 4 d. The methanol was then reduced under *vacuo* and fresh methanol- $d_4$  (36.2 g, 1.09 mol) was added. After five such successive treatments, ca 95% of the  $\alpha$  protons had been exchanged for deuterium, as determined by n.m.r. spectroscopy. The resulting mixture was distilled under reduced pressure to give the colourless liquid product. Yield 16.2 g, 43%.  
[b.p. 65 °C, 2 mm Hg;

Table E.2.1.1.  $^{13}\text{C}$ - $\{^1\text{H}\}$  n.m.r.<sup>a</sup> data for the ligand resonances in compounds (2.16a)-(2.19).

Compound	$\delta$ (Ligand Resonances)
(2.16a)	127.3 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 9.2 \text{ Hz}$ ), 128.8 (s), 133.6 (m, $J(\text{CP}) = 40.4 \text{ Hz}$ , $J(\text{CPx}) = 16.0 \text{ Hz}$ ), 134.0 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 11.9 \text{ Hz}$ ).
(2.16b)	14.6 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 28.9 \text{ Hz}$ ), 127.5 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 7.2 \text{ Hz}$ ), 129.0 (s), 130.3 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 11.1 \text{ Hz}$ ).
(2.17)	127.3 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 9.5 \text{ Hz}$ ), 128.8 (s), 133.8 (m, $J(\text{CP}) = 40.3 \text{ Hz}$ , $J(\text{CPx}) = 16.7 \text{ Hz}$ ), 134.3 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 12.4 \text{ Hz}$ , $ J(\text{CPx}) + J(\text{CPx}')  = 12.3 \text{ Hz}$ ).
(2.18a)	127.3 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 9.2 \text{ Hz}$ ), 128.8 (s), 133.8 (m, $J(\text{CP}) = 40.4 \text{ Hz}$ , $J(\text{CPx}) = 15.8 \text{ Hz}$ ), 134.3 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 12.3 \text{ Hz}$ ).
(2.19)	127.7 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 7.3 \text{ Hz}$ ), 129.2 (s), 134.0 (m, $J(\text{CP}) = 40.7 \text{ Hz}$ , $J(\text{CPx}) = 15.8 \text{ Hz}$ ), 134.5 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 9.0 \text{ Hz}$ ).

<sup>a</sup> Spectra (100.6 MHz) measured in  $\text{CDCl}_3$  at ambient temperature.

Chemical shifts ( $\delta$ ) in p.p.m. ( $\pm 0.1$ ) to high frequency of  $\text{SiMe}_4$  and coupling constants ( $J$ ) in Hz ( $\pm 0.1$ ). Multiplicities: s = singlet, m = multiplet.

$^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 220 MHz):  $\delta$ 1.96 (2H, s), 2.39 (residual protons, m), 3.68 (6H, s) p.p.m.;  
mass spec (CI)  $m/z$ : 165 [ $(\text{M}+\text{H})^+$ ].]

**Preparation of 1,5-Pentanediol-2,2,4,4- $\text{d}_4$ .** - This was prepared in a similar manner to 3,3-dimethyl-1,5-pentanediol to give a colourless liquid. Yield 80 g, 75%.

$^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 220 MHz):  $\delta$ 1.49 (2H, s), 1.84 (residual protons, m), 3.68 (4H, s), 4.81 (2H, br s), p.p.m.].

**Preparation of 1,5-Dibromopentane-2,2,4,4- $\text{d}_4$ .** - This was prepared in a similar manner to 1,5-dibromo-3,3-dimethylpentane to give a colourless liquid. Yield 5.0 g, 40%.

[b.p. 69 °C, 2 mm Hg;

$^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 220 MHz): 1.56 (2H + residual protons, m), 3.42 (4H, s) p.p.m.;

mass spec (EI)  $m/z$ : 236, 234, 232 (1:2:1) [ $\text{M}^{++}$ ].]

**Table E.2.1.2. Elemental analyses<sup>a</sup>**

Compound	C	H
$[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2)_5]$	61.97 (62.35)	5.21 (5.10)
$[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{CH}_2)_5]$	45.87 (46.57)	6.01 (5.96)
$[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$	62.95 (62.96)	5.33 (5.27)
$[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$	61.52 (63.15)	5.73 (5.42)
$[(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{CD}_2\text{CH}_2\text{CD}_2\text{CH}_2)] \cdot \text{H}_2\text{O}$	60.75 (60.66)	4.98 (4.71)

<sup>a</sup> Calculated values are given in parentheses.

Preparation of 1,5-bis(bromomagnesium)-2,2,4,4-d<sub>4</sub>-pentane. - This was prepared using a similar procedure to 1,5-bis(bromomagnesium) pentane in 90% yield.

Preparation of  $[(PPh_3)_2Pt(CH_2CO_2CH_2CO_2CH_2)]$  - A solution of 1,5-bis(bromomagnesium)-2,2,4,4-d<sub>4</sub>-pentane (5 cm<sup>3</sup>, 0.45 M in THF, 2.25 mmol) was added dropwise over 15 min to a stirred suspension of  $[PtCl_2(1,5-COD)]$  (0.374 g, 1.0 mmol) in diethylether (25 cm<sup>3</sup>) and tetrahydrofuran (15 cm<sup>3</sup>) cooled to -50 °C. The reaction mixture was then allowed to warm slowly over 30 min to 0 °C to give a pale yellow solution. The solution was then cooled to -50 °C and a solution of  $PPh_3$  (0.524 g, 2.0 mmol) in diethylether (5 cm<sup>3</sup>) was added dropwise over 5 min. The solution was then allowed to warm to ambient temperature over 45 min. Ethanol (10 cm<sup>3</sup>) was then added and the volume reduced to 10 cm<sup>3</sup> under reduced pressure. The off white solid product was then filtered off, washed with ethanol (10 cm<sup>3</sup>) and diethylether (10 cm<sup>3</sup>) and dried. The product was recrystallised by dissolving in dichloromethane (20 cm<sup>3</sup>) and ethanol (10 cm<sup>3</sup>) and this solution heated on a steam bath until the appearance of white crystals. The solution was then cooled slowly to room temperature and then to -20 °C. The white crystalline product was filtered off, washed with ethanol (10 cm<sup>3</sup>) and diethylether (10 cm<sup>3</sup>) and dried in vacuo over  $P_2O_5$ . Yield 0.79 g, 87%.

<sup>13</sup>C-<sup>1</sup>H n.m.r. data for phosphine ligand resonances given in Table E.2.1.1.



**Preparation of 2,2-Dichlorodiphenylmethanol.** - This was made according to the method of Haller *et al.*<sup>342</sup>

A solution of *o*-chlorophenylmagnesium bromide (190 cm<sup>3</sup>, 1.4 M in diethylether, 0.27 mol) was added dropwise to a vigorously stirred solution of 2-chlorobenzaldehyde (37.4 g, 0.27 mol) in diethylether (120 cm<sup>3</sup>), over a period of 1 h. The mixture was then heated under reflux for a further 2 h. Dilute hydrochloric acid was then added with care to the reaction mixture over a period of 1 h. The reaction mixture was then left to cool and the two resulting layers left to settle out. The organic layer was then separated and dried over MgSO<sub>4</sub> and filtered. The solvent was then removed under reduced pressure to give the crude orange oil product. Distillation under reduced pressure gave the yellow oil product. Yield 53.1 g, 77%.

[b.p. 140 °C, 0.1 mm Hg;

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 220 MHz): δ 2.72 (1H, br s), 6.56 (1H, s), 7.25-7.64 (6H, s) p.p.m.].

**Preparation of 2,2'-Dichlorodiphenylmethane.** - This was made using an adaptation of Marvel *et al.*<sup>274</sup> method to prepare diphenylacetic acid from benzoic acid.

A mixture of red phosphorus (8.86 g, 0.28 mol) and iodine (2.95 g, 0.012 mol) dissolved in glacial acetic acid (150 cm<sup>3</sup>) was allowed to stand for 15 min. 2,2'-Dichlorodiphenylmethanol (65.0 g, 0.26 mol) and water (2.95 cm<sup>3</sup>) were added and the resulting mixture heated under reflux for 24 h. The reaction was then filtered to remove excess of phosphorus and the filtrate poured into a stirred

solution of sodium metabisulphite (15.0 g, 0.08 mol) in water (500 cm<sup>3</sup>). The mixture was stirred for 2 h. On leaving the mixture to stand for 1 h a yellow oil settled out which was then extracted with diethylether (100 cm<sup>3</sup>). The organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent removed under reduced pressure to give the oily product. Distillation under reduced pressure gave a colourless liquid. Yield 50.9 g, 83%.

[b.p. 108 °C, 0.2 mm Hg;

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 220 MHz); δ 4.22 (2H, s) 7.12-7.51 (8H, m)

p.p.m.;

Mass spec. (EI) m/z; 236, 238, 240 (9:6:1) [M<sup>+</sup>].]

**Preparation of 2,2'-Dilithiodiphenylmethane.** - Lithium flakes (4.0 g, 0.57 mol) were suspended in diethylether (75 cm<sup>3</sup>) in a 1000 cm<sup>3</sup> flask filled with argon. The flask was fitted with a mechanical stirrer and dropping funnel and cooled to 0 °C. A solution of 2,2'-dichlorodiphenylmethane (10.80 g, 0.046 mol) in diethylether (125 cm<sup>3</sup>) was added dropwise over a period of 1 h. The resulting orange suspension was then stirred for 24 h. The reaction mixture was filtered free of the excess of lithium metal. The organolithium concentration was determined by a modification of the double titration method of Gilman: separate aliquots were quenched with water and successively with 1,2-dibromoethane and water, and titrated against 0.05 M hydrochloric acid.

Table E.2.1.3. Elemental analyses<sup>a</sup>

Compound	C	H
$[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	50.61 (50.24)	6.64 (6.75)
$[(\text{PMe}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	43.92 (44.40)	3.72 (3.50)
$[(\text{PMe}_2\text{Ph})_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	54.49 (53.63)	4.47 (5.06)
$[(\text{PPh}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	66.21 (66.43)	4.71 (4.55)
$[(1,5\text{-COD})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	54.69 (53.72)	4.47 (4.72)
$[(\text{PEt}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	35.53 (35.26)	4.71 (4.75)

<sup>a</sup> Calculated values are given in parentheses.

**Preparation of  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$**  - A solution of 2,2'-dilithiodiphenylmethane (5 cm<sup>3</sup>, 0.22 M in diethylether, 1.10 mmol) was added dropwise to a stirred suspension of  $[\text{PtCl}_2(\text{PEt}_3)_2]$  (0.374 g, 1.0 mmol) in benzene (25 cm<sup>3</sup>). The reaction mixture was then stirred for 2 h during which time the suspension had turned bright orange. Water (20 cm<sup>3</sup>) was then added and the two layers separated. The organic layer was dried over  $\text{MgSO}_4$  and then filtered. Removal of the solvent by evaporation under reduced pressure followed by addition of diethylether (40 cm<sup>3</sup>) gave the orange solid product. Recrystallisation from benzene/methanol 1:1 v/v gave a white air stable crystalline solid. Yield 0.44 g, 74%.

<sup>13</sup>C-<sup>1</sup>H n.m.r. data for phosphine ligand resonances given in Table E.2.1.3. .

**Table K.2.1.4.**  $^{13}\text{C}$ - $^1\text{H}$  n.m.r.<sup>a</sup> data for ligand resonances of compounds (2.20a-f) and (2.21).

Compound	$\delta$ (Ligand resonances)
(2.20a)	8.0 (br s), 16.6 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 28.7 \text{ Hz}$ ).
(2.20b)	17.3 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 32.2 \text{ Hz}$ ).
(2.20c)	14.7 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 32.4 \text{ Hz}$ ), 16.7 (m, $ J(\text{CPx}) + J(\text{CPx}')  = 32.3 \text{ Hz}$ ), 128.3 (t, $J(\text{CP}) = 8.9 \text{ Hz}$ ), 129.6 (s), 131.0 (t, $J(\text{CP}) = 11.0 \text{ Hz}$ ), 137.6 (m, $J(\text{CP}) = 35.8 \text{ Hz}$ ).
(2.20d)	14.6 (m, $ J(\text{C-Px}) + J(\text{CPx}')  = 32.8 \text{ Hz}$ ), 128.2 (m, $J(\text{CP}) = 10.1 \text{ Hz}$ ), 129.6 (s), 130.9 (m, $J(\text{CP}) = 11.6 \text{ Hz}$ ), 137.5 (m, $J(\text{CP}) = 41.9 \text{ Hz}$ ).
(2.20e)	127.3 (t, $J(\text{CP}) = 6.6 \text{ Hz}$ ), 129.1 (s), 133.1 (m, $J(\text{CP}) = 45.9 \text{ Hz}$ ), $J(\text{CP}) = 15.1 \text{ Hz}$ ), 134.5 (t, $J(\text{CP}) = 11.0 \text{ Hz}$ ).
(2.20f)	29.9 (s), 105.4 (t, $J(\text{CP}) = 50.5 \text{ Hz}$ ).
(2.21)	7.9 (br s), 16.1 (m)

<sup>a</sup> Spectra (100.6 MHz) measured in  $\text{CDCl}_3$  at ambient temperature. Chemical shifts

in p.p.m. ( $\pm 0.1$ ) relative to  $\text{SiMe}_4$ . Coupling constants  $J$  in Hz ( $\pm 0.1$ )

Multiplicities: s = singlet, t = virtual triplet, m = multiplet.

Preparation of  $[(PMe_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$ . - A solution of 2,2'-dilithiodiphenylmethane (11 cm<sup>3</sup>, 0.22 M in diethylether, 2.2 mmol) was added dropwise to a stirred suspension of  $[PtCl_2(PMe_3)_2]$  (0.90 g, 1.82 mmol) in benzene (40 cm<sup>3</sup>) cooled to 0 °C. The reaction mixture was then stirred for 2 h and allowed to warm up to ambient temperature. The bright yellow mixture was again cooled to 0 °C and water (25 cm<sup>3</sup>) was then added and the two layers separated. The organic layer was dried over  $MgSO_4$  and then filtered. Removal of the solvent by evaporation under reduced pressure, followed by addition of diethylether (40 cm<sup>3</sup>) gave the pale brown solid product. Recrystallisation from benzene/methanol 1:1 v/v gave a white air stable crystalline solid. Yield 0.59 g, 63%.

$^{13}C\{-^1H\}$  n.m.r. data for phosphine ligand resonances given in Table E.2.1.3. .

Preparation of  $[(PMe_2Ph)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$ . - This was prepared using a similar procedure to  $[(PMe_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$  at 0 °C from  $[PtCl_2(PMe_2Ph)_2]$  to give a pale brown solid. Yield 0.36 g, 56%.

$^{13}C\{-^1H\}$  n.m.r. data for phosphine ligand resonances given in Table E.2.1.3.

Preparation of  $[(PMePh_2)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$ . - This was prepared using a similar procedure to  $[(PMe_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$  at 0 °C from  $[PtCl_2(PMePh_2)_2]$  to give a pale brown solid. Yield 0.33 g, 49%

$^{13}C\{-^1H\}$  n.m.r. data for phosphine ligand resonances given in Table E.2.1.3.

Preparation of  $[(PPh_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$ . - This was prepared using a similar procedure to  $[(PEt_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$  from  $[PtCl_2(PPh_3)_2]$ . Recrystallisation from benzene methanol 1:1 v/v gave a white crystalline solid. Yield 0.33 g 62%.

$^{13}C$ - $\{^1H\}$  n.m.r. data for phosphine ligand resonances given in Table E.2.1.3. .

Preparation of  $[(1,5-COD)Pt(\overline{C_6H_4CH_2C_6H_4})]$ . - A solution of 2,2'-dilithiodiphenylmethane (9.0 cm<sup>3</sup>, 0.27 M in diethylether, 2.4 mmol) was added dropwise to a stirred suspension of  $[PtCl_2(1,5-COD)]$  (0.8 g, 2.14 mmol) in diethylether (40 cm<sup>3</sup>) cooled to -78 °C. The mixture was then stirred for 2 h. Methanol (20 cm<sup>3</sup>) was then added and the mixture allowed to warm to ambient temperature over 30 min. The volume was reduced to 10 cm<sup>3</sup> by evaporation under reduced pressure. The yellow solid product was filtered off, washed with methanol (25 cm<sup>3</sup>) and diethylether (30 cm<sup>3</sup>) and dried in vacuo over  $P_2O_5$ . Yield 1.2 g, 84%.

$^{13}C$ - $\{^1H\}$  n.m.r. data for phosphine ligand resonances given in Table E.2.1.3.

Preparation of  $[(dppm)Pt(\overline{C_6H_4CH_2C_6H_4})]$ . - A solution of diphenyl phosphinomethane (0.115 g, 0.30 mmol) in dichloromethane (10 cm<sup>3</sup>) was added to a stirred solution of  $[(1,5-COD)Pt(\overline{C_6H_4CH_2C_6H_4})]$  (0.150 g, 0.32 mmol) in dichloromethane (25 cm<sup>3</sup>). The mixture was then stirred for 1 h. The solvent was removed by evaporation under reduced pressure. The residue was triturated with diethylether (40 cm<sup>3</sup>) to give the pale yellow solid product. Recrystallisation

from benzene/ethanol 1:1 v/v gave a white solid. Yield 0.20 g.  
93%.

**Preparation of  $[(dpe)Pt(\overline{C_6H_4CH_2C_6H_4})]$ .** - This was prepared using a similar procedure to  $[(dppm)Pt(\overline{C_6H_4CH_2C_6H_4})]$  to give a white air stable solid. Yield 0.21 g, 92%.

**Treatment of  $[(PEt_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$  with Triphenylcarbenium tetrafluoroborate.** - A solution of  $[(PEt_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$  (0.050 g, 0.084 mmol) in benzene- $d_6$  (2.5 cm<sup>3</sup>) was treated with  $Ph_3CBF_4$  (0.033 g, 0.10 mmol) under an atmosphere of nitrogen. The resulting mixture was left to stand for 5 min and then examined by  $^1H$  and  $^{31}P$ -( $^1H$ ) n.m.r. spectroscopy. Further aliquots (up to 10 mol equivalent) were added over a period of 2 d and the resulting mixtures examined again by  $^1H$  and  $^{31}P$ -( $^1H$ ) n.m.r. spectroscopy.

**Treatment of  $[(PEt_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$  with Methylolithium, Butyllithium, tert-Butyllithium and Lithium bis(trimethylsilyl)-amide.** - A solution of  $[(PEt_3)_2Pt(\overline{C_6H_4CH_2C_6H_4})]$  (0.050 g, 0.084 mmol) in benzene- $d_6$  (2.5 cm<sup>3</sup>) was treated with aliquots of the basic reagent (0.10 mmol) under an atmosphere of nitrogen. The resulting mixture was left to stand for 15 min and then examined by  $^1H$  and  $^{31}P$ -( $^1H$ ) n.m.r. spectroscopy. Further aliquots (up to 10 mol equivalent) were added over a period of 2 d and the resulting mixtures again examined by  $^1H$  and  $^{31}P$ -( $^1H$ ) n.m.r. spectroscopy.

**Treatment of  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  with Methyl Iodide.** A solution of  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (0.100 g, 0.167 mmol) in benzene- $d_6$  (2.5  $\text{cm}^3$ ) was treated with methyl iodide (10  $\mu\text{l}$ , 0.160 mmol) under an atmosphere of nitrogen. The resulting mixture was then examined by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy. Further aliquots of methyl iodide (10  $\mu\text{l}$ , 0.160 mmol) were added (up to 10.0 mol equivalent) and the mixture again examined by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy.

**Preparation of  $[(\text{PEt}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$ .** - A solution of iodine (2.08  $\text{cm}^3$ , 0.079 mmol in benzene, 0.165 mmol) in dichloromethane (15  $\text{cm}^3$ ) was added dropwise over 4 h to a stirred solution of  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (0.10 g, 0.167 mmol) in dichloromethane (40  $\text{cm}^3$ ) cooled to  $-50^\circ\text{C}$  under argon. The mixture was then stirred for a further 2 h at  $-50^\circ\text{C}$ . The solvent was then removed by evaporation under reduced pressure. Addition of ethanol (40  $\text{cm}^3$ ) gave the yellow solid product which was filtered off and washed with ethanol (15  $\text{cm}^3$ ). Recrystallisation from benzene/methanol 1:1 v/v gave a yellow air stable crystalline solid. Yield 0.132 g, 93%.  $^{13}\text{C}$ - $^1\text{H}$  N.m.r. data for phosphine ligand resonances given in Table E.2.1.3. .

**Treatment of  $[(\text{PEt}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  with Lithium bis(trimethylsilyl)amide.** - A solution of  $[(\text{PEt}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (0.050 g, 0.06 mmol) in benzene- $d_6$  was treated with  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$  (0.1  $\text{cm}^3$ , 1.6 M in hexane, 0.1 mmol) under an atmosphere of nitrogen. The resulting mixture was left to stand for 15 min and then examined by



$^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectroscopy. Further aliquots (up to 10 mol equivalent) were added over a period of 12 h and the reaction mixture again examined by  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectroscopy.

**Treatment of  $[(\text{PEt}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  with tert-Butyllithium.** - A solution of  $[(\text{PEt}_3)_2\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (0.05 g, 0.06 mmol) in benzene- $d_6$  (2.5  $\text{cm}^3$ ) was treated with  $\text{Bu}^t\text{Li}$  (0.1  $\text{cm}^3$ , 1.6 M in pentane, 0.1 mmol) under an atmosphere of nitrogen. The resulting mixture was examined by  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectroscopy. Further aliquots (up to 10 mol equivalent) were added over a period of 12 h and the reaction mixture again examined by  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectroscopy.

**Treatment of  $[(\text{dppm})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  with Iodine.** - A solution of  $[(\text{dppm})\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (0.025 g, 0.034 mmol) in benzene- $d_6$  (2.0  $\text{cm}^3$ ) was treated with a solution of iodine (0.42  $\text{cm}^3$ , 0.079 M in benzene, 0.034 mmol) under an atmosphere of nitrogen. On leaving the solution to stand for 10 min, the colourless solution turned dark orange. The resulting mixture was examined by  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectroscopy.

**Treatment of  $[(\text{dppm})\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  with tert-Butyllithium.** - A solution of  $[(\text{dppm})\text{I}_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$  (0.033 g, 0.034 mmol) in benzene- $d_6$  (2.5  $\text{cm}^3$ ) was treated with  $\text{Bu}^t\text{Li}$  (0.1  $\text{cm}^3$ , 1.6 M in pentane, 0.16 mmol). The resulting mixture was examined by  $^{31}\text{P}-\{^1\text{H}\}$  n.m.r. spectroscopy.

## E.2.2 X-RAY CRYSTAL STRUCTURE DATA

Crystal Structure Analysis of  $[(Ph)_2Pt(CH_2)_5]$  and  $[(Ph)_2Pt(CH_2CH_2C(CH_3)_2CH_2CH_2)]$ . - For both compounds, data were collected with a Syntex  $P_{21}$  four circle diffractometer for 2 $\theta$  in the range 3-50°. Background intensities were measured at each end of the scan for 0.25 s of the scan time. Three standard reflections, monitored every 200 reflections, showed slight changes during data collection; the data were rescaled to correct for this. The density was measured by flotation. Unit cell dimensions and standard deviations were obtained by least squares fit to 15 high angle reflections. Refinement used the observed reflections  $[I/\sigma(I) \geq 3.0]$  corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Details for each compound are given in Table E.2.2.1.

Heavy atoms were located by Patterson methods and the remaining lighter atoms by successive Fourier synthesis. Anisotropic temperature factors were used for all atoms except hydrogens which were inserted at fixed positions and not refined ( $U = 0.07 \text{ \AA}^2$ ). Methyl groups were treated as rigid  $CH_3$  units with their initial orientation taken from the H-atom peaks on a difference Fourier synthesis. Final refinement of  $F$  was by cascaded least squares methods. A weighting scheme of the form  $W = 1/(\sigma^2(F) + g^2)$  was applied. Computing used SHELXLT (Sheldrick, 1983)<sup>343</sup> on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were taken from the International Tables (1974).<sup>344</sup>

Table E.2.2.1. Crystal Data and Data Collection Conditions.

Compound	$[(\text{Pw}_6\text{P}_6)_2\text{Pt}(\text{CH}_2)_5]$	$[(\text{Pw}_6\text{P}_6)_2\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_3]$
Formula	$\text{C}_{21}\text{H}_{32}\text{P}_6\text{Pt}$	$\text{C}_{23}\text{H}_{36}\text{P}_6\text{Pt}$
Crystal System	Triclinic	Triclinic
Systematic Absences	None	None
Space Group	$P_1$	$P_1$
a/Å	9.569 (3)	9.615 (4)
b/Å	9.956 (2)	10.097 (3)
c/Å	13.712 (4)	13.835 (6)
$\alpha/^\circ$	68.97 (2)	71.06 (3)
$\beta/^\circ$	70.40 (2)	74.22 (3)
$\gamma/^\circ$	64.35 (2)	73.87 (3)
U/Å <sup>3</sup>	1084.8 (5)	1195.7 (8)
Dc/gcm <sup>-3</sup>	1.66	1.58
Dm/gcm <sup>-3</sup>	1.53	1.44
Z	2.00	2.00
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	66.8	60.6

Table E.2.2.1. (continued).

Compound	$[(\text{Ph}_2\text{P})_2\text{Pt}(\text{CH}_3)_2]$	$[(\text{Ph}_2\text{P})_2\text{Pt}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)]$
$\nu_{000}$	532	531.87
Crystal size/mm	0.10X0.20X0.63	0.44X0.43X0.81
Max. transmission factor	0.63	0.47
Min. transmission factor	0.43	0.19
Scan range about $K\alpha_1$	-1.0/+1.0	-1.1/+1.1
Reflections collected	3645	4216
Reflections observed $[I/\sigma(I) \geq 3.0]$	2721	3252
Weighting constant: $g$	0.00003	0.00078
$R(\text{final})$	0.0545	0.0500
$R_w(\text{final})$	0.0471	0.0523
Max. on final difference Fourier	1.8	3.0
Min. on final difference Fourier	-1.8	-1.5
Max $d/\sigma$ (final cycle)	0.32	0.48

Suitable crystals of compound  $[(PMe_2Ph)_2Pt(CH_2)_5]$  were obtained by recrystallisation from dichloromethane/methanol 2:1 v/v. The crystals formed were yellow irregular plates.

In the determination, anisotropic temperature factors were used for all non-H atoms apart from the atoms of the pentamethylene ring. It was found that four of the carbon atoms of the ring were disordered, each having a major and a minor position. Their linked occupancies were refined as a single population parameter which converged to 0.664 and 0.336 for the major and minor components respectively.

Colourless flaky crystals of compound  $[(PMe_2Ph)_2Pt(CH_2CH_2C(CH_3)_2CH_2CH_2)]$  were obtained from dichloromethane/methanol 2:1 v/v. The crystals had a strong tendency for satellites to be attached, and several crystals had to be examined to obtain a suitable single crystal. The one selected contained one principal component with a satellite giving approximately 3% of the diffraction intensity of the main crystal.

**Crystal Structure Analysis of  $[(PEt_3)_2Pt(C_6H_4CH_2C_6H_4)]$  and  $[HPEt_3)_2Pt(C_6H_4CH_2C_6H_4)]$ .** - For both compounds, the data were collected and refined as above. Details for each compound are given in Table K.2.2.2.

Suitable crystals of compound  $[(PEt_3)_2Pt(C_6H_4CH_2C_6H_4)]$  were obtained by recrystallisation from benzene/methanol 1:1 v/v. The crystals formed were irregular shaped colourless plates.

Orange red plate crystals of compound  $[(PEt_3)_2Pt(C_6H_4CH_2C_6H_4)]$  were obtained by recrystallisation from

benzene/methanol 1:1 v/v. For compound  $[(\text{PEt}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$   
the refinement of the observed reflections  $[I/\sigma(I) \geq 3.0]$  did not  
include correction for absorption effects.

Table E.2.2.2. Crystal Data and Data Collection Conditions.

Compound	$[(\text{PEt}_3)_3\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	$[(\text{PEt}_3)_3\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_7)]$
Formula	$\text{C}_{25}\text{H}_{40}\text{P}_3\text{Pt}$	$\text{C}_{25}\text{H}_{40}\text{P}_3\text{Pt}$
Crystal System	Monoclinic	Monoclinic
Systematic Absences	h0l: h+1=2n+1 Ok0: k=2n+1	h0l: 1=2n+1 Ok0: k=2n+1
Space Group	$P2_1/\text{nc}$	$P2_1/c$
a/Å	10.7482 (20)	17.3750 (51)
b/Å	15.2587 (39)	9.6810 (27)
c/Å	14.8849 (39)	19.1924 (51)
$\alpha/^\circ$	89.99 (2)	89.98 (2)
$\beta/^\circ$	90.77 (2)	120.72 (2)
$\gamma/^\circ$	89.98 (2)	90.02 (2)
U/R <sup>3</sup>	2440.9 (1.0)	2775.4 (13)
Dc/gcm <sup>-3</sup>	1.60	2.04
Dm/gcm <sup>-3</sup>	1.53	1.44
$\chi$	4.00	4.00
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	61.79	76.41

Table E.2.2.2. (continued).

Compound	$[(\text{FeC}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$	$[(\text{FeC}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$
$F_{000}$	1191.73	1615.73
Crystal size/cm	$0.043 \times 0.033 \times 0.048$	
Max. transmission factor	0.61	-
Min. transmission factor	0.21	-
Scan range about $K_{\alpha 1}\text{-X}_{\alpha 2}/^\circ$	$-1.05/+1.05$	$-1.1/+1.1$
Reflections collected	4768	5415
Reflections observed [ $I/I(1) \geq 3.0$ ]	2725	3311
Weighting constant: $k$	0.0079	0.00292
$R(\text{final})$	0.0476	0.0533
$R_w(\text{final})$	0.0476	0.0561
Max. on final difference Fourier	2.53	2.83
Min. on final difference Fourier	-1.95	-2.12
Max $d/e$ (final spec)	0.38	0.107



### E3. PREPARATION OF ALCOHOL- AND ALKOXO- COMPLEXES OF PLATINUM(II) AND PALLADIUM (II)

Preparation of  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH}$ . - Triphenylphosphine (20.0 g, 0.076 mol) and lithium flakes (2.80 g, 0.40 mol) were placed in a 250 cm<sup>3</sup> flask filled with nitrogen. Dry tetrahydrofuran (150 cm<sup>3</sup>) was slowly added to the stirred mixture which was cooled to -15 °C. The resulting mixture was then stirred for 6 h and allowed to warm to +20 °C. The red solution was then filtered free of excess of lithium metal and cooled to -70 °C. 1-Chloropropan-3-ol (6.5 cm<sup>3</sup>, 7.4 g, 0.078 mol) was added dropwise by syringe over 10 min. After the addition was complete the mixture was then allowed to warm to ambient temperature over 1 h during which time the red colour disappeared. Water (100 cm<sup>3</sup>) was then added and the resulting two layers were separated. The aqueous layer was extracted with tetrahydrofuran (3 x 50 cm<sup>3</sup>) and the combined organic layers dried over  $\text{MgSO}_4$  and then filtered. Removal of the solvent under reduced pressure gave the white solid product which was recrystallised from petroleum ether (b.p. 100-120 °C). Yield 14.5 g, 78%.

$^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 220 MHz);  $\delta$  1.56 (2H, m), 2.08 (2H, m.) 2.21 (1H, br m), 3.63 (2H, t,  $J = 8$  Hz) 7.18-7.52 (10H, m) p.p.m.  
 $^{31}\text{P}$ - $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 162 MHz);  $\delta$  -16.1 p.p.m.  
 $^{13}\text{C}$ - $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 22.6 MHz);  $\delta$  24.5 (1C, d,  $J(\text{CP})=10.3$  Hz), 29.4 (1C, d,  $J(\text{CP})=14.7$  Hz), 63.3 (1C, d,  $J(\text{CP})=13.2$  Hz), 128.8 (2C, s), 130.5 (4C, s), 133.7 (4C, s), 139.0 (2C, d,  $J(\text{CP})=13.2$  Hz) p.p.m.

I.R. ( $\text{cm}^{-1}$ );  $\nu$  (O-H) 3400br,  $\nu$  (P-Ph) 1435s,  $\nu$  (C-O) 1050m;

Mass spec. (C.I.)  $m/z$ : 245  $[(M+H)^+]$

Found: C, 73.66; H, 6.95; Calc. for  $C_{15}H_{17}O$  P: C, 73.75; H, 7.02%.

**Preparation of  $[PtCl_2(Ph_2PCH_2CH_2CH_2OH)_2]$ .** - A solution of  $Ph_2PCH_2CH_2CH_2OH$  (0.27 g, 1.12 mmol) in dichloromethane (5 cm<sup>3</sup>) was added dropwise over 15 min to a stirred suspension of  $[PtCl_2(1,5-COD)]$  (0.215 g, 0.57 mmol) in dichloromethane (10 cm<sup>3</sup>). The mixture was then stirred until all the solid had dissolved. Evaporation of the solvent, followed by addition of diethylether (10 cm<sup>3</sup>) gave the white solid product which was washed with diethylether (30 cm<sup>3</sup>) and dried in vacuo. Yield 0.41 g, 96%.

**Preparation of  $[PtBr_2(Ph_2PCH_2CH_2CH_2OH)_2]$ .** - This was prepared using a similar procedure to  $cis-[PtCl_2(Ph_2PCH_2CH_2CH_2OH)_2]$  from  $[PtBr_2(1,5-COD)]$  to give a pale yellow solid. Yield 0.38 g, 95%.

**Preparation of  $[PtI_2(Ph_2PCH_2CH_2CH_2OH)_2]$ .** - This was prepared using a similar procedure to  $cis-[PtCl_2(Ph_2PCH_2CH_2CH_2OH)_2]$  from  $[PtI_2(1,5-COD)]$  to give a bright yellow solid. A mixture of cis and trans isomers was obtained (9 : 1 c/t). Yield 0.40 g, 92%.

**Preparation of cis- $[Pt(CH_3)_2(Ph_2PCH_2CH_2CH_2OH)_2]$ .** - This was prepared using a similar procedure to  $[PtCl_2(Ph_2PCH_2CH_2CH_2OH)_2]$  from  $[Pt(CH_3)_2(1,5-COD)]$  to give a white solid. Yield 0.29 g, 90%.

Table E.3.1. Elemental Analyses<sup>a</sup>

Compound	C	H
$[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$	46.96 (47.72)	4.61 (4.54)
$[\text{PtBr}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$	43.06 (42.72)	4.25 (4.06)
$[\text{PtI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$	37.29 (38.43)	3.95 (3.65)
$[\text{Pt}(\text{CH}_3)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$	54.88 (53.85)	5.91 (5.65)
$[\text{PtCl}(\text{CH}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$	50.64 (50.72)	5.00 (5.08)
$[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$	53.92 (54.11)	4.98 (5.15)
$[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2](\text{ClO}_4)_2$	40.50 (40.83)	3.78 (3.88)
$[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$	51.57 (52.86)	5.48 (4.73)

<sup>a</sup> Calculated values are given in parentheses.

Preparation of trans- $[\text{PtCl}(\text{CH}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$ . - This was prepared using a similar procedure to  $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  from  $[\text{PtCl}(\text{CH}_3)](1,5\text{-COD})$  to give a white solid. Yield 0.27 g, 83%.

Preparation of trans- $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$ . - This was prepared using a similar procedure to  $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  from  $[\text{PdCl}_2(\text{Bu}^t\text{CN})_2]$  to give a bright yellow solid. Yield 0.28 g, 96%.

Preparation of  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2](\text{ClO}_4)_2$ . - A solution of  $\text{AgClO}_4$  (0.25 g, 1.2 mmol) in methanol (5 cm<sup>3</sup>) was added dropwise

over 15 min to a stirred solution of cis-[PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] (0.20 g, 0.26 mmol) in methanol (30 cm<sup>3</sup>); a white precipitate formed immediately. The mixture was stirred for 2 h and then evaporated to dryness under reduced pressure. The residue was then extracted with dichloromethane (3 x 20 cm<sup>3</sup>) and the solution filtered twice. The volume was then reduced to 10 cm<sup>3</sup> and diethylether (15 cm<sup>3</sup>) added slowly to precipitate the white solid product. The white solid was filtered off and washed with diethylether (15 cm<sup>3</sup>). Yield 0.178 g, 75%.

**Preparation of cis-[Pt(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>].** - A solution of NaOH (1.7 cm<sup>3</sup>, 0.76 M in methanol, 1.32 mmol) was added dropwise over 15 min to a stirred solution of cis-[PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] (0.25 g, 0.33 mmol) in methanol (20 cm<sup>3</sup>). On addition of the base the solution turned pale yellow. The mixture was then stirred for 2 h and then evaporated to dryness under reduced pressure. The residue was then extracted with dichloromethane (2 x 20 cm<sup>3</sup>) and the solution filtered. The volume was reduced to 5 cm<sup>3</sup> and petroleum ether (b.p. 40-60 °C) (2 cm<sup>3</sup>) was added and the mixture left at 0 °C for 16 h. The white solid product was filtered off and washed with diethylether (10 cm<sup>3</sup>) and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. Yield 0.18 g, 82%.

#### PRELIMINARY N.M.R. EXPERIMENTS

**Treatment of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] with PPhCl<sub>2</sub>.** - A solution of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] (0.025 g, 0.033 mmol) in chloroform-d<sub>1</sub>

(2.0 cm<sup>3</sup>) was treated with a solution of PPhCl<sub>2</sub> (0.125 cm<sup>3</sup>, 0.26 M in dichloromethane, 0.033 mmol). The resulting mixture was examined by <sup>31</sup>P-<sup>1</sup>H n.m.r. spectroscopy. Triethylamine (ca 0.2 cm<sup>3</sup>) was then added to the mixture. White fumes were observed. The mixture was again examined by <sup>31</sup>P-<sup>1</sup>H n.m.r. spectroscopy.

**Treatment of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] with Sodium Methoxide.** - A solution of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] (0.025 g, 0.033 mmol) in methanol-d<sub>4</sub> (1.5 cm<sup>3</sup>) was treated with sodium methoxide (40 μl, 0.78 M in methanol, 0.032 mmol). The resulting mixture was examined by <sup>31</sup>P-<sup>1</sup>H n.m.r. spectroscopy. Further aliquots of sodium methoxide (40 μl) were added successively and the progress of the reaction followed by <sup>31</sup>P-<sup>1</sup>H n.m.r. spectroscopy. On the addition of 2 mol equivalents of the base a further aliquot of sodium methoxide (0.8 cm<sup>3</sup>, 0.6 mmol) was added. The resulting mixture was examined by <sup>31</sup>P-<sup>1</sup>H n.m.r. spectroscopy.

**Treatment of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] with Triethylamine in methanol.** - A solution of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] (0.025 g, 0.033 mmol) in methanol-d<sub>4</sub> (2.0 cm<sup>3</sup>) was treated with an excess of triethylamine (0.5 cm<sup>3</sup>). The resulting mixture was examined by <sup>31</sup>P-<sup>1</sup>H n.m.r. spectroscopy.

**Treatment of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] with Triethylamine in chloroform.** - A solution of [PtCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] (0.025 g, 0.033 mmol) in chloroform-d<sub>3</sub> (2.0 cm<sup>3</sup>) was treated with an excess of triethylamine (0.5 cm<sup>3</sup>). The resulting mixture was examined by

$^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy. The mixture was then cooled to  $-60^\circ\text{C}$  and examined again by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy.

**Treatment of  $[\text{PtBr}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  with Sodium Methoxide.** - A solution of  $[\text{PtBr}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  (0.03 g, 0.036 mmol) in methanol- $d_4$  (1.0  $\text{cm}^3$ ) was treated with a solution of sodium methoxide (1.0  $\text{cm}^3$ , 0.78 M in methanol, 0.78 mmol). On leaving the solution to stand for 10 min the pale yellow solution turned colourless. The resulting mixture was examined by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy.

**Treatment of  $[\text{PtI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  with Sodium Methoxide.** - A solution of  $[\text{PtI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  (0.03 g, 0.032 mmol) in methanol- $d_4$  (1.0  $\text{cm}^3$ ) was treated with a solution of sodium methoxide (1.0  $\text{cm}^3$ , 0.78 M in methanol, 0.78 mmol). On leaving the solution to stand for 10 min the bright yellow solution had turned colourless. The resulting mixture was examined by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy.

**Treatment of  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2](\text{ClO}_4)_2$  with Triethylamine.** - A solution of  $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  (0.07 g, 0.093 mmol) in methanol- $d_4$  (1.5  $\text{cm}^3$ ) was treated with an excess of  $\text{AgClO}_4$  (0.10 g, 0.5 mmol) in methanol (1.5  $\text{cm}^3$ ). The white precipitate was filtered off and the filtrate treated with an excess of triethylamine (0.5  $\text{cm}^3$ ). The resulting mixture was examined by  $^{31}\text{P}$ - $^1\text{H}$  n.m.r. spectroscopy.

Treatment of  $[\text{PtCl}(\text{CH}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  with Sodium Methoxide. -

A solution of  $[\text{PtCl}(\text{CH}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  (0.03 g, 0.04 mmol) in methanol- $d_4$  (1.0  $\text{cm}^3$ ) was treated with a solution of sodium methoxide (1.0  $\text{cm}^3$ , 0.78 M in methanol, 0.78 mmol). The resulting mixture was examined by  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy.

Treatment of  $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  with Sodium Methoxide. - A

suspension of  $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$  (0.03 g, 0.45 mmol) in methanol- $d_4$  (1.0  $\text{cm}^3$ ) was treated with a solution of sodium methoxide (1.0  $\text{cm}^3$ , 0.78 M in methanol, 0.78 mmol). On addition of the base the bright yellow suspension dissolved to give a yellow solution which was examined by  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy.

Treatment of  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$  with Hydrochloric Acid. - A

solution of  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$  (0.03 g, 0.044 mmol) in methanol- $d_4$  (2.5  $\text{cm}^3$ ) was treated with an excess of 6 M hydrochloric acid (0.2  $\text{cm}^3$ ). The resulting mixture was examined by  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy.

Treatment of *cis*- $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$  with  $\text{SO}_2$ . - Sulphur dioxide

gas was bubbled through a solution of  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$  (0.030 g, 0.044 mmol) in methanol- $d_1$  (2.5  $\text{cm}^3$ ) for 30 min. The resulting mixture was examined by  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy.

Treatment of  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$  with 2,6-Dimethylphenyl

isocyanide. - A solution of  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{O})_2]$  (0.02 g, 0.036 mmol) in methanol- $d_4$  (2.5  $\text{cm}^3$ ) was treated with one equivalent of

2,6-dimethylphenylisocyanide (0.28 cm<sup>3</sup>, 0.12 M in methanol, 0.033 mmol). The resulting mixture was examined by <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectroscopy. A second equivalent of 2,6-dimethylphenylisocyanide (0.28 cm<sup>3</sup>, 0.033 mmol) was added to the mixture which was then examined by <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectroscopy.



## E.4.1 PREPARATION OF ACETYLIDE COMPLEXES OF THE TYPE



Preparation of  $K_2[Pt(C\equiv CPh)_4]$ . - Butyllithium (6.25 cm<sup>3</sup>, 1.6 M in hexane, 10 mmol) was added dropwise over 20 min to a stirred solution of PhC≡CH (1.23 cm<sup>3</sup>, 10 mmol) in tetrahydrofuran (10 cm<sup>3</sup>) cooled to -78 °C. The mixture was stirred for 15 min and then  $[PtCl_2(SMe_2)_2]$  (0.39 g, 1.0 mmol) was added. The mixture was stirred for 1 h and allowed to warm to ambient temperature. Water (30 cm<sup>3</sup>) was then added and the two resulting layers were separated. The volume of the aqueous layer was reduced to 10 cm<sup>3</sup>. A solution of KCl (0.74 g, 10 mmol) in water (5 cm<sup>3</sup>) was added. The mixture was then stirred for 1 h. The white solid product was filtered off, washed with ethanol (20 cm<sup>3</sup>) and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. Yield 0.51 g. 76%.

Preparation of  $K_2[Pt(C\equiv C^tBu)_4]$ . - Butyllithium (6.25 cm<sup>3</sup>, 1.6 M in hexane, 10 mmol) was added dropwise over 20 min to a stirred solution of Bu<sup>t</sup>C≡CH (1.23 cm<sup>3</sup>, 10 mmol) in tetrahydrofuran (10 cm<sup>3</sup>) cooled to -78 °C. The mixture was stirred for 15 min and then  $[PtCl_2(SMe_2)_2]$  (0.39 g, 1.0 mmol) was added and the mixture was stirred for 1 h and allowed to warm to ambient temperature. Water (30 cm<sup>3</sup>) was then added and the two resulting layers were separated. The volume of the aqueous layer was reduced to 10 cm<sup>3</sup>. A solution of KCl (0.74 g, 10 mmol) in water (5 cm<sup>3</sup>) was added and the mixture was then stirred for 1 h. The white solid product was filtered off, washed with ethanol (20 cm<sup>3</sup>) and dried in vacuo over

$P_2O_5$ . Yield 0.450 g, 76%.

**Preparation of  $[N(PPh_3)_2]_2Pt(CsCOO_2CH_3)_4$ .** - Butyllithium (6.25 cm<sup>3</sup>, 1.6 M in hexane, 10 mmol) was added dropwise over 15 min to a stirred solution of  $CH_3CO_2C\equiv CH$  (0.92 cm<sup>3</sup>, 10 mmol) in tetrahydrofuran (20 cm<sup>3</sup>) cooled to -78 °C. The mixture was stirred for 3 h and allowed to warm to -40 °C. After cooling the mixture to -78 °C, methanol (30 cm<sup>3</sup>) was added. The mixture was then stirred for a further 3 h and allowed to warm to ambient temperature. The volume was reduced to 30 cm<sup>3</sup> and a solution of  $[N(PPh_3)_2]Cl$  (1.2 g, 2 mmol) in methanol (20 cm<sup>3</sup>) was then added. The mixture was stirred for 3 h and then the off white solid product was filtered off and washed with methanol (25 cm<sup>3</sup>) and diethylether (25 cm<sup>3</sup>) and dried in vacuo over  $P_2O_5$ . Yield 0.46 g, 77%.

**Preparation of  $[N(PPh_3)_2]_2[Pt(CsCOO_2CH_2CH_3)_4]$ .** - This was prepared using a similar procedure to  $[N(PPh_3)_2]_2[Pt(CsCOO_2CH_3)_4]$  to give a cream solid. Yield 0.540 g, 82%.

#### E.4.2. Electrochemistry of $K_2[Pt(CsCPh)_4]$ and $K_2[Pt(CsCbu^t)_4]$

All cyclic voltammetry measurements were made using a conventional three electrode system with a Pt counter electrode, saturated calomel (S.C.E) reference electrode with a Pt or glassy carbon (Oxford electrodes), working electrode.

The potentiostat used was a purpose built instrument and voltammograms were recorded on a Bryan 60000 series X/Y, + recorder. All measurements were carried out at room temperature.

The water was from a Millipore milliQ water purification system and all electrolytes were of Analar quality or were recrystallised before use. Acetonitrile was spectroscopic grade (Fisons) and freshly distilled from calcium hydride before use.

#### E.4.3. X-RAY CRYSTAL STRUCTURE DATA

**Crystal Structure Analysis of  $K_2[Pt(C\equiv CMe)_4]$ .** Data were collected with a Syntex  $P_{21}$  four circle diffractometer for  $2\theta$  in the range  $50^\circ$ . Background intensities were measured at each end of the scan for 0.25 s of the scan time. Three standard reflections monitored every 200 reflections, showed slight changes during data collection; the data were rescaled to correct for this. Unit cell dimensions and standard deviations were obtained by least squares fit to 15 high angle reflections. Refinement used the 3054 observed reflections  $[I/\sigma(I) \geq 3.0]$  corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Details of the data collection parameters are given in Table E.4.3.

Heavy atoms were located by Patterson methods and the remaining lighter atoms by successive Fourier syntheses. The platinum atom lies at special position 2a, giving  $\bar{1}$  molecular symmetry. Anisotropic temperature factors were used for all atoms except hydrogens which were inserted at fixed positions and not refined ( $U = 0.07 \text{ \AA}^2$ ). Methyl groups were treated as rigid  $CH_3$  units with their initial orientation taken from the H-atom peaks on a difference Fourier synthesis. It was found that three of the carbon atoms in one of the tert-butyl groups were disordered, each having two position. Their linked occupancies were refined as a single

population parameter. Final refinement of  $F$  was by cascaded least squares methods. A weighting scheme of the form  $W = 1/\sigma^2(F) + g(F^2)$  was applied. Computing used SHELXTL (Sheldrick, 1983)<sup>343</sup> on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were taken from the International Tables (1974).<sup>344</sup>

Suitable crystals of compound  $K_2[Pt(CsC\equiv Bu^t)_4]$  were obtained by recrystallisation from water/potassium hydroxide. The crystals formed were colourless plates but immediately lost solvent on exposure to air. The crystal was mounted in a Lindermann tube in a water-saturated atmosphere.

Table K.4.3 Crystal Data and Data Collection Conditions

Compound	$[\text{K}_2\text{Pt}(\text{CSCBu}^t)_4] \cdot 28\text{H}_2\text{O}$
Formula	$\text{C}_{24}\text{H}_{36}\text{K}_2\text{Pt} \cdot 28\text{H}_2\text{O}$
Crystal System	Monoclinic
Systematic Absences	$h0l; h+1=2n+1$ $0k0; k=2n+1$
Space Group	$P2_1/n$
$a/\text{\AA}$	11.9844
$b/\text{\AA}$	15.4744
$c/\text{\AA}$	14.9634
$\alpha/^\circ$	89.972
$\beta/^\circ$	104.212
$\gamma/^\circ$	90.032
$U/\text{\AA}^3$	2690.05
$D_c/\text{gcm}^{-3}$	1.363
$Z$	2.00
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	29.61
$F_{0000}$	1151.83
Crystal size /mm	$0.053 \times 0.042 \times 0.042$
Scan Range about $K_{\alpha 1} - K_{\alpha 2}/^\circ$	$-0.95/+0.95$
Reflections collected	5199
Reflections observed $[I/\sigma I \geq 3.0]$	3054
Weighting constant: $g$	0.000003
$R$ (final)	0.0602
$R_w$ (final)	0.533
Max. on final difference fourier	+1.88
Min. on final difference fourier	-3.15
Max $\delta/\sigma$ (final cycle)	0.35

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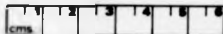
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